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PROCEEDINGS

Alkaline treatment of tin sludge

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***Abstract*— Every industrial production is associated with waste production. Electrolytic tinning produces sludge containing approximately 57 % tin. Due to the limited tin reserves and its importance for industrial use, it is appropriate to treat this sludge. This work deals with hydrometallurgical treatment of tin sludge by alkaline leaching in sodium hydroxide solutions. Experiments show that the highest tin recovery of 90% was achieved using 3M NaOH at 80 °C. The next step after the leaching process is the refining of solution and electrolytic recovery of tin.**

I. Introduction

The metallurgical industry generates a large amount of waste, the metal content of which is many times higher than in the case of primary raw materials. Such waste can include tin sludge, which may contain more than 30% tin, which makes it an interesting secondary raw material [1].

Tin surface treatment - tinning is a widespread method for treatment of steel sheets. The reason for such treatment is increased corrosion resistance. Tin on its surface forms oxides SnO and SnO_2, which are chemically resistant and do not react with the environment. There are two processes for the tinning of the steel plates: hot-dipping and electroplating [2].

Electrolytic tinning is a newer tinning process in which pure metallic tin is used as an anode and is electrolytically transferred to the surface of steel sheets. The thickness of the tin layer is 1 to 2 $g.cm^{-2}$ [2].

The electrolyte used in this process may be: phenolsulfonic acid, fluoroboric acid, methanesulfonic acid, halogen or alkaline stannic solution [3].

Due to the good anticorrosive properties of tin, tinplate has a wide range of applications from the food industry, through various packaging for tobacco products to the automotive industry [4].

Due to its specific properties, tin has been classified among 62 metals whose complete replacement with another material is not possible. Its stock is critical because of its high consumption. With a current production of 280 000 t, tin reserves are estimated to be less than 20 years. For this reason, tin has been ranked among the strategic metals by the European Union in the Strategic Energy Technology Plan [5].

Due to limited primary sources, research is focused also on extracting of the tin from waste. L. Fröhlich et al. successfully investigated the possibility of treating the tin sludge in hydrochloric acid when they managed to obtain almost 96 % tin. H. M. Henao et al. they also used hydrochloric acid but the processed material was milled solders. By leaching this waste, they managed to obtain 95 % tin [1][6].

Currently, tin is also recovered from used tin sheets. The first attempts were made in 1882. This process is carried out electrolytically in sodium hydroxide solution, where tin plate is used as the anode and the steel plate is used as cathode. Tin passes from the anode to the cathode where it is reduced as a tin sponge, which is subsequently remelted. The less used hydrometallurgical method also uses sodium hydroxide solution, but not as an electrolyte but as a leaching agent. In this process, the necessary oxidation can be achieved by adding an oxidizing agent or by continuously immersing and emerging tinplate sheets [7].

The aim of this work was to study the possibility of tin recovery from tin sludge by leaching in sodium hydroxide solution.

II. EXPERIMENT

A. *Material*

A sample of MSA tin sludge waste produced by tinning in methanesulfonic acid electrolyte was used for experiments. Fig. 1 shows the sludge before drying. Drying at 105 °C removed 25.02 % moisture. Three samples were taken from the dried sludge and subjected to AAS (atomic absorption spectrometry) chemical analysis. The average content of tin, antimony and iron is shown in Table I.

TABLE I
CONTENT OF TIN, ANTIMONY AND IRON

	Sn	**Sb**	**Fe**
Content [%]	57,27	0,72	0,49

Figure 1. Sludge sample before drying

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B. Thermodynamic study

The following chemical reactions may occur during the leaching:

$Sn + 6OH^- = Sn(OH)_6^{2-} + 4e^-$ (1)

$Sn + 2OH^- + 4H_2O = Sn(OH)_6^{2-} + 2H_2(g)$ (2)

$2Fe + 6OH^- = Fe_2O_3 + 3H_2O + 6e^-$ (3)

$Sb + 3NaOH + H_2O = Na_3SbO_4 + 2.5H_2(g)$ (4)

$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O$ (5)

$SnO_2.xH2O + 2OH^- \rightarrow [SnOH_6]^{2-} + (x - 2)H_2O$ (6)

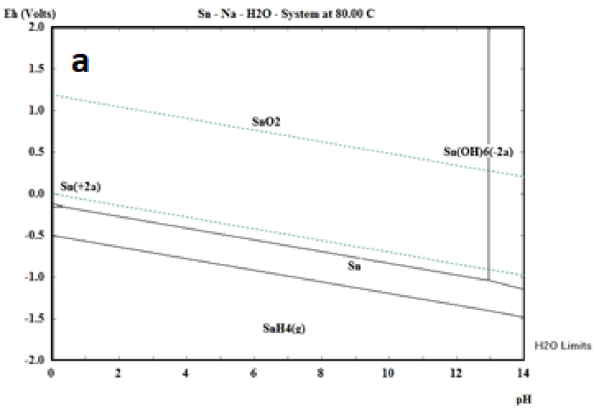
$Sn(OH)_2 + NaOH \rightarrow Na[Sn(OH)_3]$ (7)

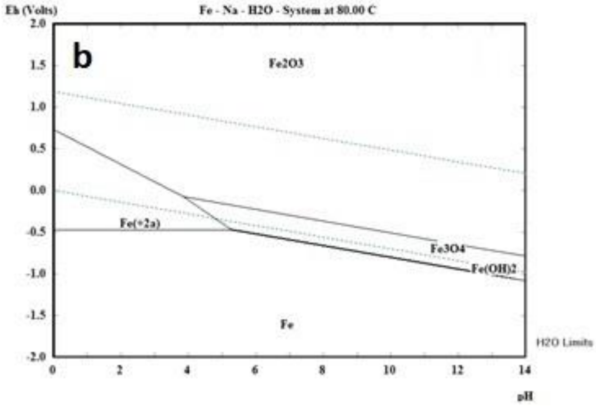
Table II shows the gibs energy values of the reactions, suggesting that reaction (1) is most likely to occur. Reaction (4) may be carried out at a temperature of up to 80 °C. No necessary thermodynamic data are available to calculate the change in the standard Gibbs energy of reactions (5), (6) and (7).

The E-pH diagrams (Fig. 2a) show that tin goes into solution at 80 °C at approximately pH = 13 in $Sn(OH)_6^{2-}$ phase. Iron, which is in the alkaline solution in the Fe_2O_3 phase, is not leachable and remains in solid form (Fig. 2b). Antimony is at pH between 10.5 and 14 in the form Na_3SbO_4 (Fig. 2c).

TABLE II
CHANGE OF STANDARD GIBBS ENERGY FOR REACTION

	ΔG[J.mol^{-1}]			
Temperature [°C]	**(1)**	**(2)**	**(3)**	**(4)**
20	-352.375	-34.531	-252.654	11.114
40	-362.896	-38.336	-259.828	6.571
60	-374.905	-42.649	-267.683	2.084
80	-388.258	-47.443	-276.138	-2.360





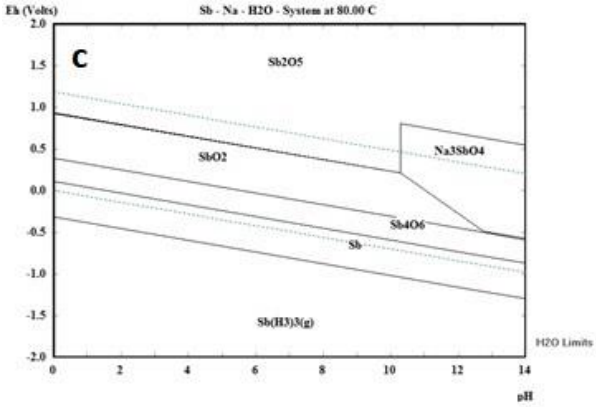


Figure 2. E-pH diagrams of Sn (a), Fe (b) and Sb (c) at 80°C

C. Methods

A 10 g sample of sludge was subjected to a set of leaching experiments in a 400 mL leaching agent solution. The leaching agent used was a 0.5 M, 1 M, 2 M, and 3 M sodium hydroxide solution. The experiments were carried out at 20 °C, 60 °C and 80 °C. In all cases, the leaching time was 60 minutes.

D. Leaching in sodium hydroxide

Fig. 3 shows tin leaching curves at 20 °C (Fig. 3a), 60 °C (Fig. 3b) and 80 °C (Fig. 3c) and various concentrations of NaOH. With increasing concentration of the solution increased the yield of tin at all temperatures. At all temperatures, the highest leaching efficiency was achieved using a 3 M NaOH solution. The leaching efficiencies of tin were 37.43 % at 20 °C, 59.58 % at 60 °C and 90.0 3% at 80 °C. As can be seen from the graphs, most of the tin leaches in the first minutes and consequently the yield only increases very slightly.

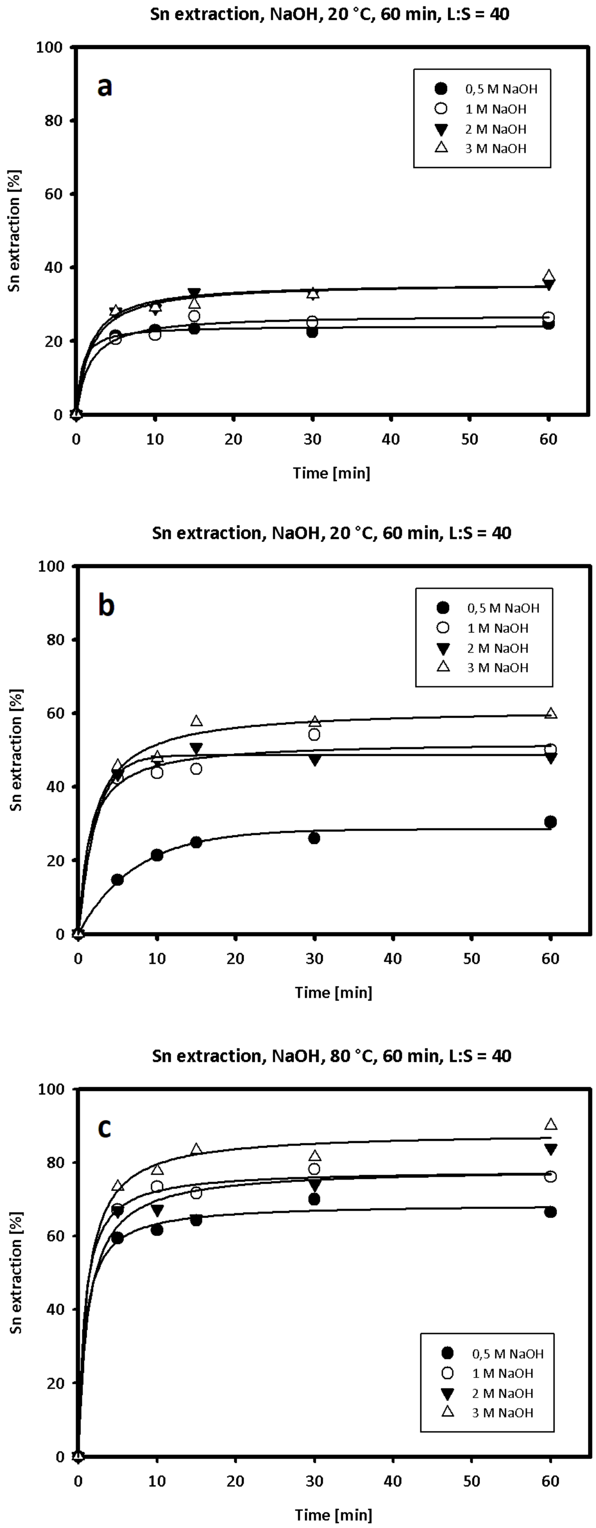


Figure 3. Extraction curves, NaOH

Fig. 4 shows significant effects on the yield of tin has a temperature for all of concentrations of NaOH used.

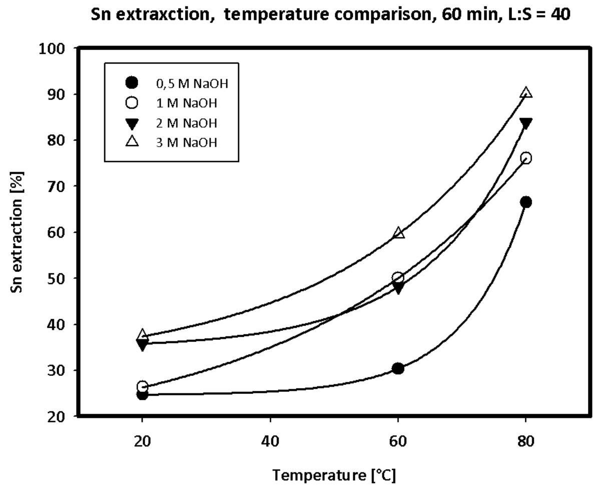


Figure 4. Influence of temperature on the Sn extraction

E. Leaching in sodium hydroxide with addition of hydrogen peroxide

Fig. 5a shows the leaching curves of tin at 20 °C using NaOH solutions (0.5 M, 1 M and 2 M) with the addition of a 10 or 40 ml H_2O_2 oxidizing agent. The highest yield of 15.78% was achieved using a 2 M NaOH solution with the addition of 10 ml H_2O_2. Fig. 5b shows the leaching curves of tin at 80 °C. 1 M and 2 M NaOH solutions were used with the addition 10 ml of H_2O_2. Higher recovery of tin (55.04 %) was achieved using 2 M NaOH.

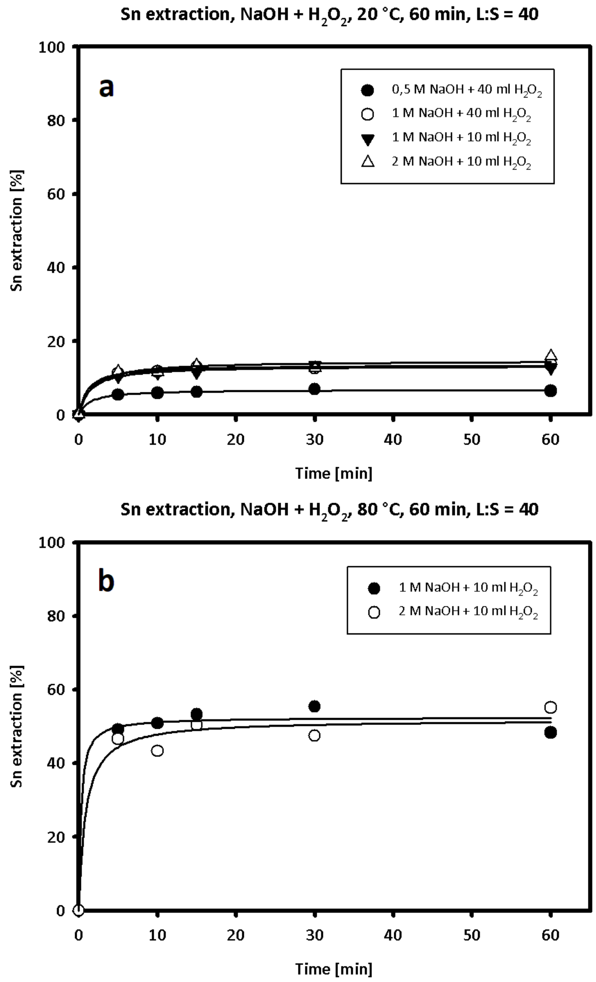


Figure 5. Extraction curves, NaOH + H_2O_2

F. Companion metals extraction

In addition to tin, antimony and iron, which are present in the tin sludge, are also leached into the solution. The recovery rate of these metals reached a maximum of 10.89 % for antimony and 2.57 % for iron. Results of leaching in sodium hydroxide are shown in TABLE III. Results of leaching in sodium hydroxide with addition of oxidizing agent (H_2O_2) are shown in Tab. IV.

III. CONCLUSION

The steel sheet has poor anticorrosion properties, therefore various surface treatments have been extended. One of the surface treatments of steel sheet is tinning. Tinplated steel is used in various sectors of industry. Various wastes are produced in the production process, including tin sludge. The sludge is collected and in a filter press excess moisture is removed. The sludge is subsequently landfilled in hazardous waste landfills or further processed to recover tin and other metals.

TABLE III
LEACHING IN SODIUM HYDROXIDE

Temperature [°C]	Concentration NaOH [M]	**Extraction [%]**	
		Sb	**Fe**
20	0,5	2,28	0,43
	1	1,62	0,68
	2	x	1,13
	3	x	1,38
60	0,5	2,87	0,33
	1	2,94	0,68
	2	3,46	0,86
	3	4,37	2,57
80	0,5	4,5	0,92
	1	7,04	0,99
	2	6,23	1,19
	3	6,11	2,22

TABLE IV
LEACHING IN SODIUM HYDROXIDE WITH ADITION OF H_2O_2

Temperature [°C]	**Concentration NaOH [M]**	**H_2O_2 [ml]**	**Extraction [%]**	
			Sb	**Fe**
20	0,5	40	x	0,27
	1	40	x	0,39
	1	10	10,32	0,70
	2	10	13,58	1,56
80	1	10	9,82	0,27
	2	10	10,89	0,76

World tin reserves are estimated to be about 20 years and therefore tin sludge, with a tin content of about 60 %, is an interesting secondary raw material. The recovery of tin negatively affects the presence of impurities that accumulate in the waste and hence pyrometallurgical treatment is not preferred. On the other hand, high purity products can be obtained by hydrometallurgical methods. Therefore, a more preferred processing option is a hydrometallurgical treatment such as leaching in hydrochloric acid or sodium hydroxide.

The results of the experiments show that the highest yield of tin (90.03 %) was achieved at 80 °C using 3 M sodium hydroxide solution.

The use of H_2O_2 as an oxidizing agent has not been shown to be appropriate since a tin yield of 55.04 % was achieved at 80 °C and 2 M NaOH solution.

In addition to tin, metals such as iron and antimony also entered the solution. Under optimal conditions for leaching of tin, the antimony yield reached 6.11 % and the iron yield 2.22 %.

The leaching results showed the possibility of treating this waste with alkaline hydrometallurgical methods. After examining the possibility of refining the solution from undesirable impurities with subsequent electrolysis, it would be possible to introduce this process also in a small scale hydrometallurgical plant in Slovakia.

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