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Production and Recycling of
Non-Ferrous Metals: Saving Resources
for a Sustainable Future

Lead • Nickel / Cobalt / Vanadium •
Minor Metals • General Pyrometallurgy •
General Hydrometallurgy • Strategies for Resource Savings •
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Ozone Assisted Leaching of Metallic Tin

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Keywords: tin, leaching, sulphuric acid, ozone

Abstract

Tin belongs to critical metals for EU mainly for energy technologies (SET-plan) and it occurs practically in all electronic devices. In an effort to save and recover this element from electric and electronic waste (WEEE) the possibility for intensification of tin leaching by use of oxidative agent – ozone was studied in this work. As the WEEE represents an extremely heterogeneous system composed of various kinds of metals and materials, experimental work was first dealing with study of pure tin metal behaviour during ozone assisted leaching. The ozone produced in ozone generator was bubbling continuously during defined time through leaching solution placed in glass reactor. The production of ozone by ozone generator (expressed in grams of O_3 per hour) as well as its solubility in sulphuric acid solutions was measured by iodometric analysis. At the beginning, the influence of sulphuric acid concentration (1 – 3 M) and temperature of solutions (20, 30, 50 °C) on ozone solubility was tested. After that, the extraction of tin (~ 5 x 3 x 1 mm cut pieces of pure metal) during leaching in sulphuric acid continuously saturated with ozone at constant flow was investigated. The influence of acid concentration, time and temperature as well as ozone flow rate on tin extraction was monitored. The extraction values for tin during leaching by use of ozone were always compared with those obtained without ozone action. Results showed that temperature of solution has detrimental effect on ozone solubility. On the contrary, acid concentration in the range of 1 – 3 M H_2SO_4 has positive effect on ozone solubility. Tin was not extracted after leaching for 2 hours in 1 M H_2SO_4 without ozone and after 6 hours of leaching in the same media the extraction represented only 2 %. However, after bubbling of ozone through the solution at ozone flow rate 7 g/hr at standard conditions (101 kPa, 20 °C), the extraction after 2 hours was enhanced to 15 % and after 5 hours increased to around 70 %. It was shown, that by presence of ozone during leaching in H_2SO_4 at standard conditions, it is possible to intensify the leaching process and tin extraction efficiency significantly. The main limiting factor of tin extraction was ozone flow during leaching. The influence of acid concentration on tin extraction was less essential. The solubility of tin species present in the solution and tin saturation during leaching played some role in the leaching process efficiency, too.

1 Theoretical

Strong oxidation potential of ozone makes it prospective in process of pretreatment and recycling of heterogeneous materials containing metals. Ozone is used in the industry as bleaching and disinfecting purposes. According to available literature data, ozone has strongly positive effect on leaching of metals in hydrometallurgical processing due to its high redox potential capable to oxidize metals to more soluble species. Although the detailed research work published in this area is still missing. One possible application of ozone is pre-treatment of composite post-consumer scrap (waste) containing polymers and metals. This means direct exposure of solid waste (scrap) to gaseous ozone which decomposes certain plastic components, thus increase the concentration of metal in by-product. The other way is to use ozone in aqueous solution, either during the leaching or during the precipitation. Known possibilities for using ozone are for example treatment of electronic waste and treatment of refractory ores, which cannot be effectively processed by traditional methods of hydrometallurgical treatment [1-2], or intensification of separation of tin and indium in the hydrometallurgical process of recycling of spent flat screens (display) [3]. Some authors claim that recycling of silver from scrap metal leaching can be carried out in the presence of ozone at ambient temperature and at low concentrations of H_2SO_4 (~ 0.1 M) [4]. The main by-product of processing is oxygen, that can be re-used in the process of ozone generation or as a leaching agent in the previous step of waste metal treatment. The results of study [4] showed that silver is dissolved in H_2SO_4 (as Ag^+) in the range of 10^{-3} to 1 M H_2SO_4 at ozone leaching, but only at lower pH value than 4. At $pH \geq 4$ the main product is insoluble Ag_2O_2 . Vinals et al. described process of silver and gold leaching from scrap metals in sulphuric acid solution in the presence of NaCl with assistance of ozone. The highest Au recovery was obtained with ozone concentration of 6.0×10^{-4} M O_3 in solution at constant temperature (25 °C), solution concentration 0.01 M H_2SO_4 , 0.05 M NaCl and a stirring speed 900 rpm. Increasing the temperature improved leaching conditions, however at 40 °C the process started to stagnate [5]. Despite the potential of ozone to enhance the hydrometallurgical recovery of metals from waste is high the ozone is not industrially used for waste processing. The further research is highly needed to clarify for which system (type of waste and leaching solution) the use of ozone starts to be beneficial. There is still lack of information about the behaviour of different metals during the ozone leaching. It is known that for ozone efficient use during leaching it is necessary to provide acidic medium (rather than alkaline), low temperature, zero or minimum catalysts or impurities (contaminants) in a solution and relatively diluted acids. Ozone solubility in solutions is especially influenced by pH, temperature, purity or character of solution, presence of catalysts, but also composition of the leaching system [6 – 7].

The aim of this work was to study the solubility of the ozone in acid solutions, and monitor the effect of ozone flow rate, temperature and concentration of sulfuric acid solutions in leaching of pure tin under standard conditions.

2 Experimental

2.1 Materials and methods

For experimental study of influence of ozone on hydrometallurgical recovery of metal (analytical grade) tin in the form bulk sample was cut to smaller pieces (~ 5 x 3 x 1 mm), Fig. 1. In the first step the solubility of ozone in solution was studied. In the second step the behaviour of tin during ozone assisted leaching in sulphuric acid solution was monitored. Preliminary test of leaching of pure metals (Ni, Cu, Sn) showed that ozone could be with advantage used at tin leaching. In this study the influence of ozone flow rate, concentration and temperature of sulphuric acid solution on tin extraction was studied. At the same time the parallel leaching of pure tin without ozone action was performed and results were together compared.

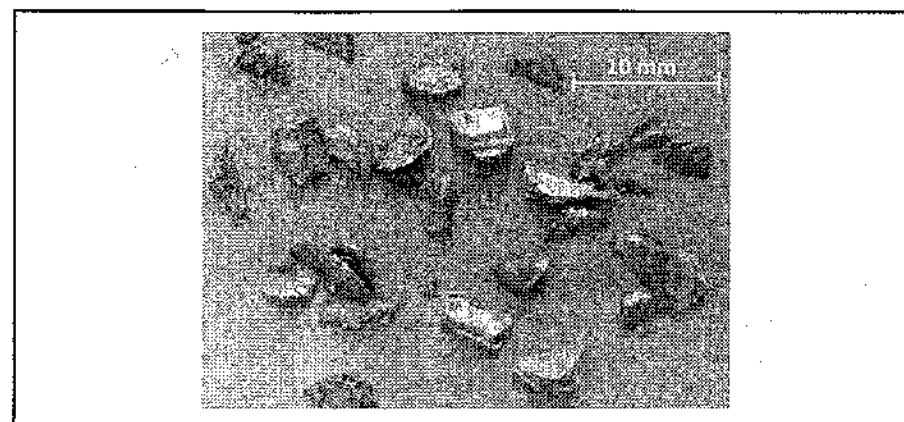


Figure 1: Experimental sample – Sn (analytical grade)

Leaching experiments were carried out in apparatus shown in Fig. 2. Experimental apparatus consists of ozone generator Q-008 with production of ozone in the range 0 – 8 g of O_3 /hr, two glass reactors, two magnetic stirrers, empty (safety) vessel for capturing of possibly deflated material and scrubbing vessel for destruction of excessive ozone. In experiments the ozone flow rates 0.3, 0.5, 3.5 and 7 g O_3 have been used. These values represent the stepping of power of ozone generator.

The produced ozone was bubbling continuously (at standard pressure) according to fixed schedule through leaching solution placed in glass reactor. The volume of KI solution was 200 ml. The production of ozone by ozone generator (expressed in grams of O_3 per hour) as well as its solubility in sulphuric acid solutions was measured by iodometric analysis. For iodometric titration the volumetric solution of sodium thiosulphate, starch indicator stabilized by $HgCl_2$ (1 g of starch, 0.005 g $HgCl_2$, 500 ml of deionized water). The volume of 1 ml consumed $Na_2S_2O_3$ solution at titration represents 2.399 mg of O_3 . The amount of ozone in the solution was calculated by equation (1):

$$m_{O_3} = \frac{\text{consumption of } Na_2S_2O_3 \times \text{volume of KI solution} \times \text{time (60 min)} \times 2.399}{\text{volume of titrated solution} \times \text{time of ozone bubbling through KI}} \quad (1)$$

In the first phase of experiments, the influence of temperature of air blown into ozonizer on ozone production was monitored. In this case the air was annealed or heated (4, 34, 41 °C) before blowing into the ozonizer by connection of vessel filled with heated or cooled water. Then the influence of sulphuric acid concentration (1 – 3 M) and temperature of solutions (20, 30, 50 °C) on ozone solubility was tested.

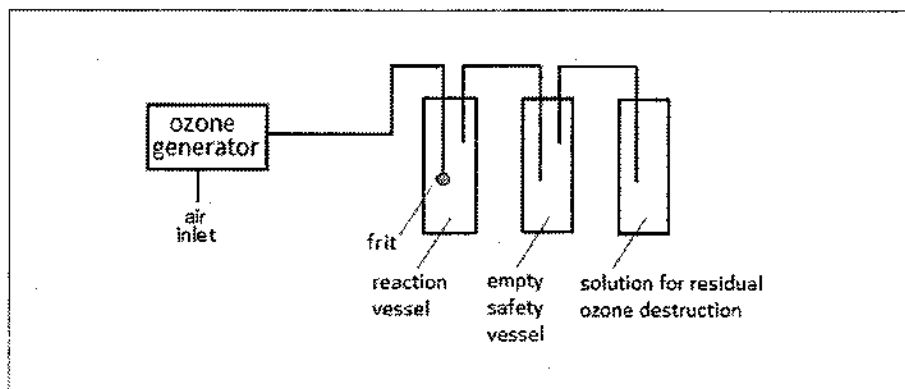


Figure2: Scheme of used leaching apparatus

In the second phase, the behaviour of elemental tin during leaching in sulphuric acid continuously saturated with ozone at constant flow was investigated. The influence of sulphuric acid concentration (1 – 3 M), time (0 – 6 hours) and solution temperature (20, 35, 50 °C) as well as ozone flow rate (0, 0.3, 0.5, 3.5, 7) on tin extraction was monitored. The extraction values for tin during leaching by use of ozone were always compared with those samples obtained without ozone action. Approximately 1 gram of metallic tin was used for each leaching experiment in 200 ml of solution and at constant mixing speed 500 rpm (magnetic stirrer was used). During experiment the liquid sample was withdrawn and analyzed for tin concentration by AAS (Varian A20++). After finishing of all experiments, the residue was filtered out, washed, dried and weight. Residue was subjected to XRD qualitative phase analysis. At the higher concentration of tin in the solution the turbidity of solution or precipitation was observed. In this case the sample has been treated before chemical analysis by dissolving them with diluted sulphuric acid (1:1) with ratio sample/acid = 0.1 – 0.25 in dependence on tin concentration in the solution.

3 Results and discussion

3.1 The solubility of ozone in solutions

Using method described in chapter 2 the ozone production (dissolute or captured in solution) in dependence on temperature of air inlet into the ozonizer, sulphuric acid concentration and temperature of acid solution was measured. In Fig.3 the influence of air temperature at ozonizer inlet on ozone production (dissolution) is shown. The ozone flow rate at 20 °C represented the value 0.45 g/hr. The ozone was captured directly within 0.5 M KI solution during interval of one minute and immediately analyzed by titrimetry. From Fig. 3 it is obvious that at temperature of around 4 °C the O₃ dissolution reaches maximum, represented 0.48 O₃/hr at given conditions. The air temperature higher than 34 °C causes rapid decreasing of O₃ production. In comparison to maximum reached value (0.48 O₃ g/hr) the O₃ production was dropped by 25 % and it represents 0.36 g/hr.

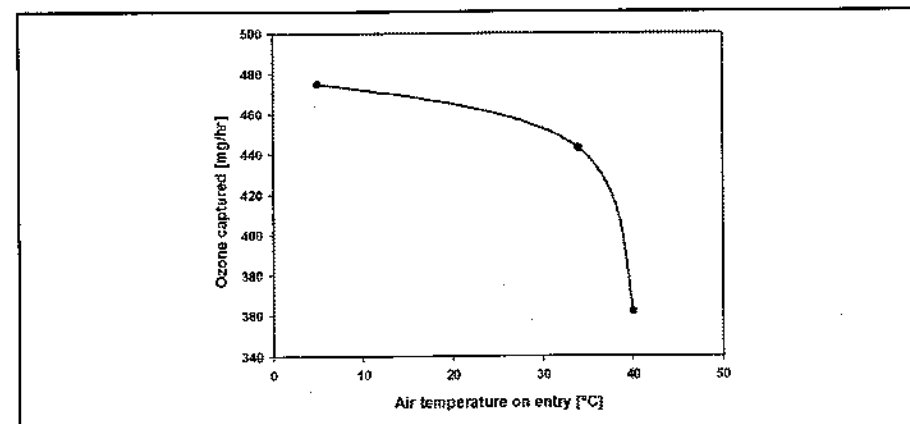


Figure 3: Influence of inlet air temperature into ozonizer on the amount of ozone captured in solution of KI

In Fig. 4a the influence of sulphuric acid concentration in the range of 1 – 3 M H₂SO₄ on amount of captured ozone is shown. The amount of captured ozone by acid solutions varies between 25 – 30 %. From these results follows that under given experimental conditions sulphuric acid solution is able to absorb only fragment of ozone available in blown atmosphere. The positive fact is that in the used narrow concentration range the influence of acid concentration on ozone solubility is not so significant. The more negative effect on ozone solubility has solution temperature, as it can be seen from Fig. 4b. At the acid solution and temperature of 50 °C, only 12 % of produced ozone was captured in 1 M sulphuric acid solution.

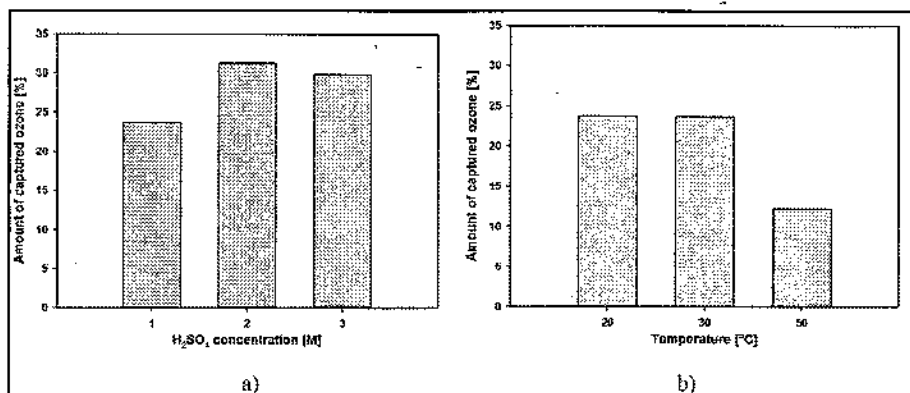


Figure 4: Ozone solubility as a function of: a) H₂SO₄ concentration; b) temperature

The obtained low efficiency of ozone capturing and dissolution in acids let to additional experiments. In order to improve the efficiency of ozone utilization in solutions, system for dispersion of ozone bubbles, shown in Fig. 5a, was changed. It was assumed that the more fine bubbles, the higher ozone solubility in a solution. The level of solution in reactor column was around 150 mm what should assure enough time to ozone become dissolved [3]. The ozone capturing efficiency in deionized water and HCl was measured, too. Fig. 5b demonstrate the effectivity of ozone capturing in various solution (H₂SO₄, HCl, deionized H₂O) by use of different frit (sintered glass).

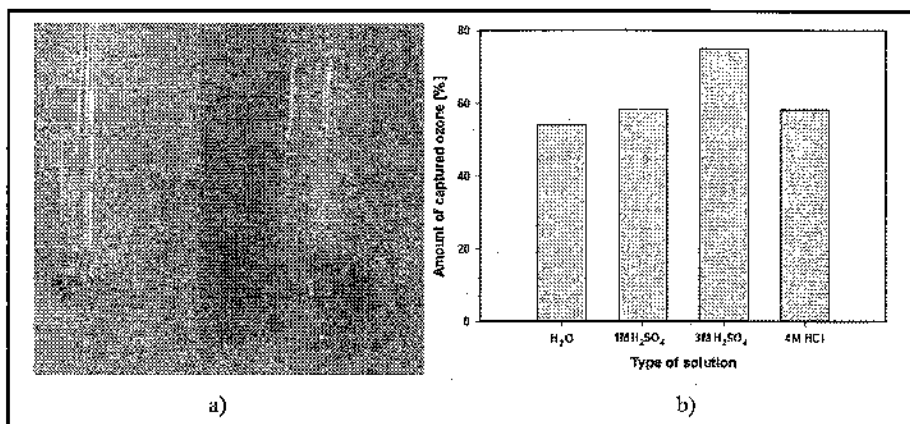


Figure 5: a) Frit used in ozone solubility measurements as function of inlet air temperature, concentration and temperature of solution (left) and type of solution (right)
b) Ozone solubility as function of solution type

3.2 Tin leaching by ozone

For studied leaching system the thermodynamic data have been calculated by use of HSC Chemistry 6.1. In Tab. 1 the potential reactions (1 - 9) of tin leaching in sulphuric acid in the presence of ozone are proposed.

Table 1: Proposed reactions for tin leaching in sulphuric acid in the presence of ozone

Reaction	T [°C]	ΔG°_{293}	$\Delta G^{\circ}_{293}/1 \text{ mol of Sn}$	#
$1.5 \text{ Sn} + \text{O}_3(\text{g}) = 1.5 \text{ SnO}_2$	20	-943.427	-628.95	1
$3 \text{ Sn} + \text{O}_3(\text{g}) = 3 \text{ SnO}$	20	-919.130	-306.37	2
$3 \text{ Sn} + \text{O}_3(\text{g}) + 3 \text{ H}_2\text{O} = 3 \text{ Sn(OH)}_2$	20	-927.316	-309.105	3
$1.5 \text{ Sn} + \text{O}_3(\text{g}) + 3 \text{ H}_2\text{O} = 1.5 \text{ Sn(OH)}_4$	20	-881.116	-587.41	4
$1.5 \text{ Sn} + \text{O}_3(\text{g}) + 3 \text{ H}_2\text{SO}_4 = 1.5 \text{ Sn(SO}_4)_2 + 3 \text{ H}_2\text{O}$	20	-926.891	-617.927	5
$\text{SnO}_2 + 2 \text{ H}_2\text{SO}_4 = \text{Sn(SO}_4)_2 + 2 \text{ H}_2\text{O}$	20	11.024	11.024	6
$3 \text{ SnO} + 6 \text{ H}_2\text{SO}_4 + \text{O}_3(\text{g}) = 3 \text{ Sn(SO}_4)_2 + 6 \text{ H}_2\text{O}$	20	-934.651	-311.55	7
$3 \text{ Sn(OH)}_2 + 6 \text{ H}_2\text{SO}_4 + \text{O}_3(\text{g}) = 3 \text{ Sn(SO}_4)_2 + 9 \text{ H}_2\text{O}$	20	-926.465	-308.821	8
$\text{Sn(OH)}_4 + 2 \text{ H}_2\text{SO}_4 = \text{Sn(SO}_4)_2 + 4 \text{ H}_2\text{O}$	20	-8.666	-8.666	9

The probability of reaction progress is given by value of ΔG° and from obtained values it is obvious that all proposed reactions except of reaction (6) are able to proceed under given conditions. The lower ΔG° represents the higher probability of reaction course. The reactions (1) and (5) have the highest probability to proceed. E-pH diagram of the system Sn-S-H₂O (Fig. 6) shows that the form of tin in solution is not much influenced by pH change. In the whole area of water stability at 20 °C tin is present in the form of tin sulphate. At lower redox potentials tin can form also SnO₂.

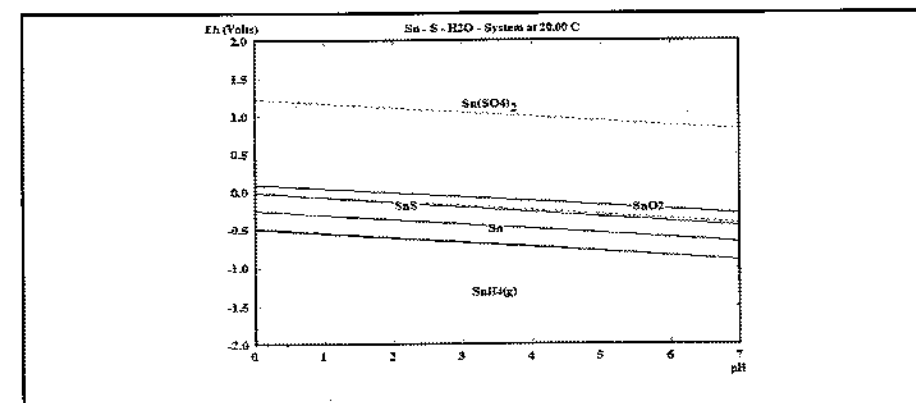


Figure 6: E-pH diagram for system Sn-S-H₂O at 20 °C

In the case of pure tin leaching, from Fig. 7a it is visible linear growth in Sn extraction in the beginning of leaching. After 1 hour the extraction kinetics of Sn was increased rapidly from around 3 to 15 % after 2 hours.

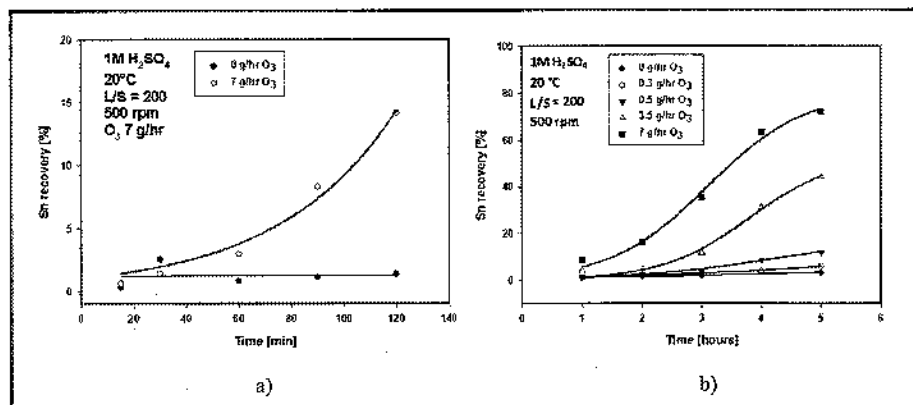


Figure 7: a) Leaching kinetics of tin with and without ozone
b) Extraction of Sn in dependence on time and O_3 flow rate

In Fig. 7b the influence of ozone flow rate on Sn extraction is shown. Low ozone flow rate, 0.3 g O_3 per hour exhibits the low tin extraction (up to 5 %), similar to value obtained at leaching without ozone action. At flow rate over 0.5 g O_3 /hr the leaching process starts to progress. The most effective leaching was reached at the highest ozone flow rate of 7 g O_3 /hr and maximum tin extraction 70 % was reached. Obtained results are listed also in Tab. 2.

Table 2: Leaching results for pure tin leached with and without O_3 at various flow rate

Time [hr]	Without O_3	0.3 [g O_3 /hr]	0.5 [g O_3 /hr]	3.5 [g O_3 /hr]	7 [g O_3 /hr]
1	0.89	1.31	1.29	2.19	8.72
2	1.24	2.44	2.68	6.99	16.23
3	2.10	2.98	4.08	16.69	35.16
4	3.38	4.06	8.85	22.82	63.44
5	2.86	5.85	12.09	22.64	71.96

The extraction of tin after 5 hours was discontinued and it could be explained by starting precipitation due to its saturation in solutions or by creating the protective layer of tin oxide. In the liquid samples withdrawn in individual time intervals (Fig. 8) it can be seen the turbidity of solution (white or yellow precipitates). It can be supposed that precipitates starts to create after the time when whole ozone is removed (decomposed) from solution and redox potential decrease. At these conditions tin starts to precipitate as tin (IV) oxide (white color) and/or in the form of tin sulphate (yellow color) in dependence on tin and acid concentration, pH and redox potential. Both of precipi-

tates were captured at the end of leaching after leaching liquor filtration. White precipitate was formed also during washing step of solid residue on the filtration paper. Yellow precipitate creates during leaching at higher temperatures and at room temperature at higher tin concentrations in the solution. Observation showed that with increasing of tin concentration in solution during leaching lead to higher turbidity and more precipitate formation.

Tin oxide is not soluble in water, but soluble in sulphuric acid, that is why the samples were treated with hot H_2SO_4 (10 M) before analysis for tin (by AAS) in order to dissolve the precipitate. Both of precipitates create only in the case of ozone assisted leaching.

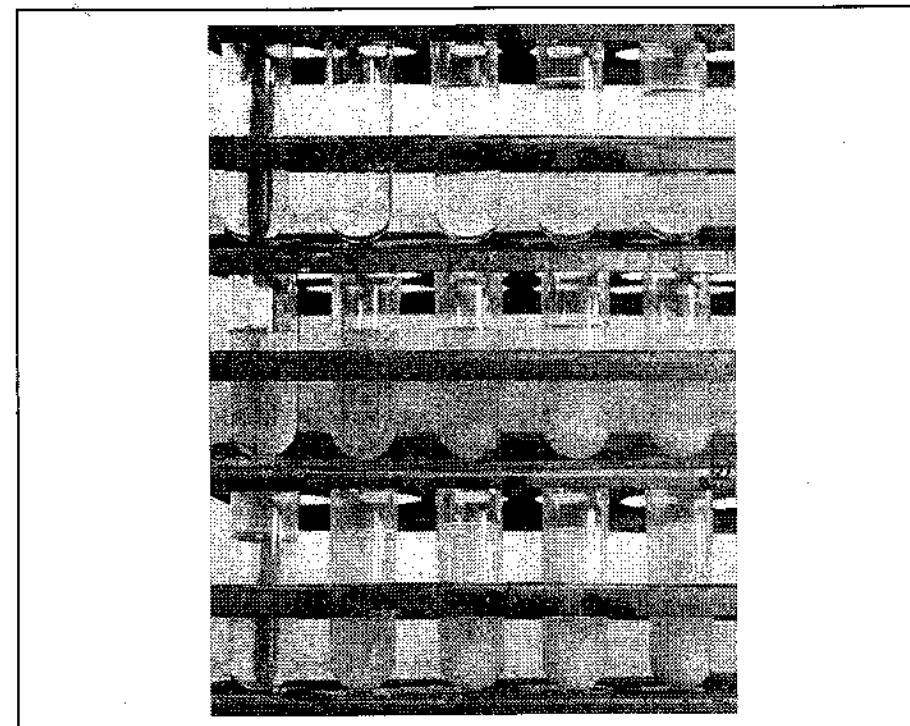


Figure 8: Evolution of turbidity during leaching (1 M H_2SO_4 , 20 °C, L/S = 200, 500 rpm):
a) without precipitate (0 g/hr O_3); b) precipitation (3.5 g/hr O_3), c) settling of precipitate (7 g/hr O_3)

Based on obtained tin leaching results (Fig. 7), in the next experiments the leaching time was prolonged for 6 hours and the higher concentrations of acid were used. By increasing the acid concentration the extraction efficiency of tin increased too, as it is visible in Fig. 8a. The tin extraction was 60 % by using 1 M H_2SO_4 after 6 hours of process and rises to 69 % in 2 M H_2SO_4 and reached

maximum 84 % in 3 M H₂SO₄. Despite of the presented negative effect of acid concentration on ozone dissolution it was shown that solution 3 M sulphuric acid has no negative effect on leachability and ozone action. Redox potential measurement in each solution (1, 2, 3 M H₂SO₄) after ozone saturation confirmed the similar values ~ 930 mV.

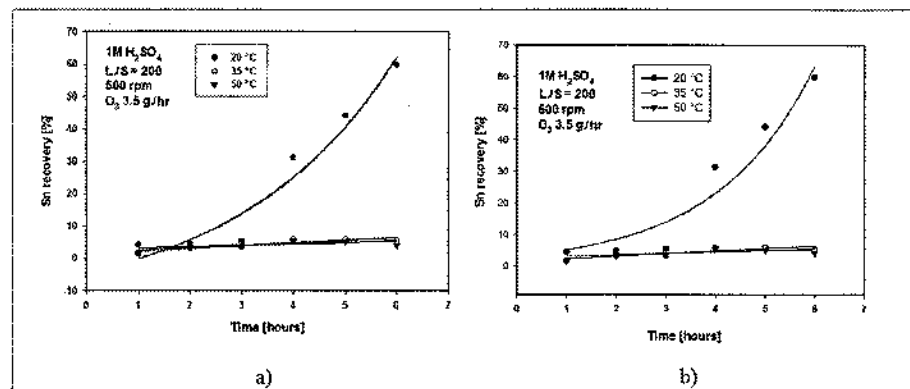


Figure 9: a) The effect of time and acid concentration on Sn extraction
b) The effect of time and solution temperature on Sn leaching

The higher leaching temperature has detrimental effect on tin extraction (Fig. 9b). Already at temperatures higher than 35 °C the effect of ozone on extraction of tin was totally eliminated. Results have been similar to those obtained for leaching without ozone. The amount of tin transferred into the solution did not exceed 5 %. It was confirmed that temperature plays crucial role in leaching process with use of ozone.

4 Conclusion

The solubility of ozone in solution is the key factor influencing the kinetics and efficiency of metal leaching. Experiments showed that solubility of ozone in acid solutions is influenced mainly by temperature. The temperature of solution above 30 °C slows down the solubility of ozone. The positive finding was that sulphuric acid in concentration range (1 – 3 M) has no negative effect on ozone solubility. However, except of character of solution (pH, composition, impurities etc.) and temperature, the solubility of ozone is influenced also by used ozone pressure (at which is blown into the solution), by level of solution in the reactor column, effectivity of ozone bubbles dispersion etc. From this point of view, the effectivity of ozone capturing and solubility in used solution could be partially improved by adjusting experimental conditions.

Experiments of tin leaching by ozone showed that:

- by increasing of ozone flow rate the extraction efficiency of tin was increased, too,
- the maximum tin extraction (70 %) was obtained at the highest ozone flow rate (7 g O₃/hr),
- increasing sulphuric acid concentration from 1 M to 3 M positively affect tin extraction. The tin extraction increased from 60 % to 84 % by using 1M and 3 M H₂SO₄, respectively,
- higher temperature of solution (above 30 °C) has detrimental effect on tin extraction and eliminates the ozone contribution in metallic tin leaching process.

Leaching mechanism of tin in sulphuric acid could take place by three different ways, either by formation of tin oxide (SnO, SnO₂), hydroxide (Sn(OH)₂) followed by leaching of these products in sulphuric acid in the presence of ozone or leached directly of metallic tin in sulphuric acid saturated with ozone. Based on thermodynamic data and obtained results it is supposed that during leaching the phase SnO could be created as semi-product rather than SnO₂. SnO₂ should neither be leached in sulphuric acid (reaction 6) neither in sulphuric acid in the presence of ozone. On the other hand, SnO₂ could create mainly after whole ozone destruction (removal) in solution when continuous ozone bubbling was stopped and redox potential dropped down (Fig. 6). Tin sulphate was created predominantly in solutions which exceed the saturation value of this compound in given solutions. Except of dissolution rate of ozone in used leaching solution the other factor influencing the overall kinetics of metallic tin leaching seems to be the formation of semi-product during leaching process in sulphuric acid. For total tin extraction into solution it is probably necessary to increase the concentration of sulphuric acid to at least 3 M, increase the ozone flow rate above 3.5 g/hr and/or prolong the leaching time. The problematic aspect of tin leaching was also the level of solubility of tin species in sulphuric acid (precipitation occurred).

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References

- [1] GONZALES-ANAYAJA. et. al: Use of Ozone for Gold Extraction from a Highly Refractory Concentrate, *Ozone: Science & Engineering: The Journal of the International Ozone Association*, 2011, 33:1, s. 42-49, DOI: 10.1080/01919512.2011.536507
- [2] OZONE TREATMENT FOR CYANIDE EFFLUENTS IN MINING INDUSTRIES, online, Available at: <<http://www.xylemwatersolutions.com/scs/canada/en-ca/products/treatment/Ozone-oxidation/Documents/Ozone%20Treatment%20for%20Cyanide%20Ef%E1%BC%80uents%20in%20Mining%20Industries%20white%20paper.pdf>>
- [3] PARK J. et.al: The Removal of Tin from ITO – scrap via Ozonization, *Bulletin Korean Chemical Society* 2009, Vol. 30, [online], Available at: <<http://dx.doi.org/10.5012/bkcs.2009.30.12.3141>>
- [4] VINALS J. et.al: Leaching of metallic silver with aqueous ozone, *Hydrometallurgy* 76, 2005, 225- 232
- [5] VINALS J. et.al: Leaching of gold and palladium with aqueous ozone in dilute chloride media, *Hydrometallurgy* 81, 2006, p. 142- 151
- [6] HORVATH M., BILITZKY L., HUTTNER J.: *Ozone*, Akademiai Kiado, Budapest, 1985, ISBN 963 05 3358 8, 333
- [7] HAVLIK T.: The acid oxidizing leaching of chalcopyrite and the behaviour of the sulfur in the process, Doctoral thesis, Technical University of Kosice, 1996, 291

Treatment of a leach liquor after leaching EAF dust

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Keywords: Electric arc furnace dust (EAF dust), hydrometallurgy, zinc, recycling, waste

Abstract

The work deals with recovery of metallic zinc from leach liquor after leaching EAF dust. The leach liquor after leaching EAF dust in sulfuric acid solutions, containing Fe 3.34 g/L, Zn 4.17 g/L, Ca 0.6 g/L and other minor metals (Cd, Pb, Cu), was processed by iron precipitation, cementation of other accompanying metals and subsequent zinc electrowinning. Goethite and jarosite processes were used as iron precipitation step. Influence of a neutralizing agent (1 M NaOH, CaCO₃ and lime milk), pH (2.5 - 4) and temperature (80 and 95 °C) on the process efficiency was investigated. The aim was to determine optimal conditions at which residual iron concentration after precipitation does not exceed 30 µg/ml; i.e. the limit for iron concentration in an electrolyte for zinc electrowinning. It was observed, that pH value and neutralizing agent have the most significant effect on the iron precipitation efficiency. Lime milk was determined as the most suitable neutralizing agent, where the residual iron concentration (80 °C, pH 4) was below 1 µg/ml, and representing precipitation efficiency of 99.98 %. After iron precipitation step, cementation of other impurities (Cd, Pb, and Cu) by zinc powder was carried out. The influence of pH and temperature on the cementation efficiency was investigated. The results showed that almost 100 % Cd and 90 % Pb can be removed by cementation. In zinc electrowinning step, the influence of temperature (20, 40 and 60 °C) and current density (333 – 1000 A/m²) on the current efficiency was studied. Maximum recovery of zinc (almost 99 %) was obtained at 40 °C and current density of 333 A/m². At these conditions, zinc was recovered as a compact plate with a minimum of zinc being precipitated in dendritic form. Results of this study show possibility to recover high purity product by processing impure zinc containing solution coming from EAF dust leaching.