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BIOLOGICAL AND CHEMICAL LEACHING OF NON-FERROUS AND PRECIOUS METALS FROM ELECTRONIC SCRAP

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ABSTRACT. A sample of mixed electronic scrap from different sources was milled to a particle size less than 100 microns and was subjected to leaching by means of different leach solutions in reactors with mechanical stirring. The best results were achieved when the scrap was initially leached be means of acidified ferric sulphate solutions to solubilize the non-ferrous metals (mainly copper, zinc, and nickel). These solutions were generated as a result of the oxidation of ferrous ions in bioreactor with immobilized chemolithotrophic bacteria. Metal extractions over 98 % were achieved within 120 hours of leaching by means of such solutions. The dissolved metals can be recovered by means of solvent extraction/electrowinning or by means of precipitation as the relevant sulphides. The solid residue after the acidic leaching was washed out by water and was subjected to alkaline thiosulphate leaching to solubilize gold and silver. 98.1 % of the gold and 97.4 % of the silver were solubilized within 72 hours. The pregnant solution after leaching was treated by means of cementation with powdered metallic zinc to precipitate these precious metals as mixed gold-silver concentrate.

БИОЛОГИЧНО И ХИМИЧНО ИЗЛУГВАНЕ НА ЦВЕТНИ И БЛАГОРОДНИ МЕТАЛИ ОТ ЕЛЕКТРОНЕН СКРАП

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РЕЗЮМЕ. Проба от смесен електронен скрап от различни източници бе смлян до размер на частиците под 100 микрона и бе подложена на излугване посредством различни излугващи разтвори в реактори с механично разбъркване. Най-добрите резултати бяха постигнати когато скрапът бе отначало излужен посредством подкиселени разтвори на феросулфат, за да се разтворят цветните метали (главно мед, цинк и никел). Тези разтвори бяха генерирани в резултат на окисление на ферийони в биореактор с имобилизирани хемолитотрофни бактерии. Посредством такива разтвори за 120 часа излугване бе постигнато извличане на металите над 98 %. Разтворените метали могат да бъдат извлечени посредством екстракция с органични реагенти и електролиза или посредством утаяване като съответните сулфиди. Твърдият остатък след излугването в кисела среда бе промит с вода и бе подложен на алкално излугване с тиосулфат, за да се разтворят златото и среброто. 98.1 % от златото и 97.4 % от среброто бяха разтворени за 72 часа. Продукционните разтвори след излугването бяха обработени посредством цинков прах (Zn^0), за да се утаят благородните метали като смесен златно-сребърен концентрат.

Introduction

An essential tendency of the present-day mineral industry is the development of methods and technologies for recycling the valuable components present in tailings from mining, mineral processing, metallurgy and different secondary industries. Some of these technologies such as bioleaching of non-ferrous metals (mainly copper) from dumps consisting of mining wastes are largely applied in commercial scale (Rossi, 1990). Technologies for utilization of smelting, converter and electronic furnace slag, pyritic cinders, coal ashes, etc are also available. Some of these technologies are based on the ability of different microorganisms, mainly acidophilic chemolithotrophic bacteria, to leach metals present in these tailings (Genchev and Groudev, 1981, 1982; Briand et al., 1991; Krebs et al., 1999; Macedo et al., 2001; Matlakovska et Sklodowska, 2001).

Some data about the possibilities to extract non-ferrous and precious metals from a mixed electronic scrap, originated from different sources, by means of a combined biological and chemical leaching are present in this paper.

Materials and methods

The sample of electronic scrap used in this study originated from different sources such as computers, printers and copy-machines. The lacquer covering the metal layers in the individual pieces of scrap was removed by means of chemical treatment. Then the individual pieces were mixed and crushed to a particle size less than 100 microns. The crushed mixture was homogenized and an average sample was used in the experimental work. Data about the chemical composition of this sample are shown in Table 1, and data about its essential acid-base properties are shown in Table 2.

Table 1
Chemical composition of the electronic scrap used in this study

Element	Content, g/kg
Cu	20.3
Zn	1.7
Ni	0.37
Pb	1.7
Fe	7.3
Al	5.9
Ca	28.4
Si	9.9
S	1.0
Au	0.132
Ag	0.482

Table 2
Acid-base properties of the electronic scrap

Parameters	Values
pH (in H_2O)	7.7
Sulphur, %	0.10
Sulphide sulphur, %	< 0.01
Alkaline oxides, %	4.1
Net neutralization potential, kg $CaCO_3$/ t	73

The finely ground material was subjected to leaching in reactors with mechanical stirring. Leach solutions with different composition were used in these experiments:

- Acidified ferric sulphate solutions generated as a result of the prior bacterial oxidation of ferrous ions to the ferric state by means of pure cultures of the iron-oxidizing acidophilic chemolithotrophs *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* as well as by mixed cultures of these bacteria. These solutions contained different concentrations of Fe^{3+} ions (in the range from 1 – 15 g/l) and of living bacterial cells;
- Acidified ferric sulphate solutions with the same concentrations of Fe^{3+} ions but without bacteria;
- Nutrient medium 9K (Silverman and Lundgren, 1959) with 9 g/l Fe^{2+} (as ferrous sulphate) inoculated by the above-mentioned bacterial cultures;
- Nutrient medium K (with the same composition as the nutrient medium 9K) but without its own energy source, i.e. without Fe^{2+} ions. The reactor containing this nutrient medium and ground electronic scrap was inoculated with the above-mentioned bacterial cultures at the start of the leaching experiment;
- Nutrient medium K supplemented by S^0 (10 g/l) and inoculated with sulphur-oxidizing chemolithotrophs *At. ferrooxidans* and *At. thiooxidans*;
- Sterile nutrient medium K (without bacteria);
- Water solutions of sulphuric acid in different concentrations (from 2-10 g/l).

The leaching was carried out at 20% pulp density and 37°C. pH was maintained at different values (from 1.7-2.5) by addition of sulphuric acid. The progress of the leaching was followed by analysis of liquid samples for dissolved metals, including ferrous, ferric and total iron species, as well as for pH, Eh, and number of chemolithotrophic bacteria.

After the end of the acidic leaching the solid residues were washed several times with distilled water to about neutral pH and then were treated with an alkaline solution to solubilized gold and silver. This solution contained microbial protein hydrolysate – 1.0 g/l, thiosulphate ions (added as ammonium thiosulphate) – 0.1 mol/l, copper ions (added as copper sulphate) – 0.005mol/l, sulphite ions – 0.01 mol/l, and ammonia to maintain the pH during leaching in the range of 10.0–10.5. The protein hydrolysate was a mixture consisting of protein hydrolysates from biomass of three different microbial species. The hydrolysates contained different gold-complexing amino acids and were mixed together in suitable proportions.

The leaching of precious metals from the solid residues was carried out in reactor with mechanical stirring at 20% pulp density and 37 °C. The pregnant solutions containing the dissolved gold and silver were treated by cementation with powdered metallic zinc to precipitate these metals as mixed gold-silver concentrates.

Elemental analysis of the liquid samples was carried out by means of atomic adsorption spectrophotometry and induced coupled plasma spectrophotometry. Elemental analysis of the solid samples was carried out by digestion and measurement of the ion concentrations in solution by the above-mentioned methods.

The isolation, identification and enumeration of microorganisms were carried out by methods described elsewhere (Karavaiko et al., 1988; Groudev, 1990).

Results and discussion

The results obtained from the acidic leaching of the electronic scrap revealed that the ferric ions were the main agent connected with the solubilization of the non-ferrous metals. The growth of the iron-oxidizing bacteria *At. ferrooxidans* and *L. ferrooxidans* in suspensions initially containing only electronic scrap as energy source depended on the generation of ferrous ions from the scrap as a result of the chemical solubilization of metallic iron (Fe^0) by the sulphuric acid present in the leach solution (Table 3).The generation of these ions initially proceeded at a low rate due to the low acidity of the leach solution and the low efficiency of the molecular oxygen as oxidizing agent towards the metallic iron. However, the generation rate steadily increased in the course of time due to bacterial oxidation of ferrous ions to the ferric state. The ferric ions efficiently oxidized the non-ferrous metals and iron present in the scrap in their zero-valent forms and turned them into the relevant soluble ions. The iron-oxidizing bacteria were not able to oxidize directly the zero-valent forms of metals and only regenerated the real oxidizing agent, i.e. the ferric ions. Due to the highly positive net neutralization potential of the electronic scrap, the bacterial activity was possible only in the cases when sulphuric acid was added from outside to maintain the pH of the leach suspensions within the acidic range suitable for these bacteria (approximately between 1.5 and 3.5). Some of these bacteria (*At. ferrooxidans* and *At. ferrooxidans*) oxidized the elemental sulphur added to the leach suspension to sulphuric acid but the acidity increased in this way only slightly improved the extraction of metals.

Table 3
Leaching of non-ferrous metals from the electronic scrap by means of bacteria growing in the presence of the scrap

Microorganisms and energy source	Metals solubilized within 120 hours, %		
	Cu	Zn	Ni
At. ferrooxidans grown on:			
-scrap + Fe^{2+}	40.1	52.9	59.0
-scrap + S^0	4.1	6.4	7.7
-only scrap	2.1	3.7	4.4
L. ferrooxidans grown on:			
-scrap + Fe^{2+}	42.0	54.1	58.7
-only scrap	2.3	3.9	4.6
At. ferrooxidans grown on:			
-scrap + S^0	4.8	8.0	9.5
-only scrap	1.7	3.2	4.1
Mixed cultures grown on:			
-scrap + Fe^{2+}	46.4	60.4	68.4
-scrap + S^0	5.9	10.0	12.0
-only scrap	3.7	6.8	8.4

Better results were obtained in experiments in which the leach suspensions contained Fe^{2+} ions added from outside (as ferrous sulphate) (Table 4).

Table 4
Leaching of non-ferrous metals from the electronic scrap by means of bacteria growing in leach suspensions containing Fe^{2+} added from outside in different concentrations.

Microorganisms and Fe^{2+}	Metals solubilized within 120 hours, %		
	Cu	Zn	Ni
At. ferrooxidans + Fe^{2+}			
0 g/l Fe^{2+}	2.1	3.7	4.4
3 g/l Fe^{2+}	24.4	35.0	42.2
9 g/l Fe^{2+}	40.1	52.9	59.0
15 g/l Fe^{2+}	52.1	66.2	72.1
L. ferrooxidans + Fe^{2+}			
0 g/l Fe^{2+}	2.3	3.9	4.6
3 g/l Fe^{2+}	25.3	36.1	44.0
9 g/l Fe^{2+}	42.0	54.1	58.7
15 g/l Fe^{2+}	51.9	65.3	72.5
Mixed culture + Fe^{2+}			
0 g/l Fe^{2+}	3.7	6.8	8.4
3 g/l Fe^{2+}	28.0	41.9	49.1
9 g/l Fe^{2+}	46.4	60.4	68.4
15 g/l Fe^{2+}	59.1	75.2	82.4

In these cases the iron-oxidizing bacteria generated ferric ions, which then oxidized the zero-valent metals to the relevant soluble ions. The efficiency of solubilization of non-ferrous metals in these systems depended on the concentration of Fe^{2+} ions added from outside. The mixed bacterial cultures showed higher leaching ability than the pure cultures of the iron-oxidizing species *At. ferrooxidans* and *L. ferrooxidans*. This was connected with the higher ferrous-oxidizing ability of these mixed cultures. They contained *At. ferrooxidans* and *L. ferrooxidans* as the prevalent species and very small quantities of *At. thiooxidans* and some heterotrophs (mainly such related to the genus *Acidiphilium*). The ratio between *At. ferrooxidans* and *L. ferrooxidans* depended on the pH of the system. At pH higher than 2.1 *At. ferrooxidans* was the prevalent microorganisms but at pH lower than 2.0 *L. ferrooxidans* was present at higher densities.

The highest extractions of non-ferrous metals were achieved in experiments in which the leach solutions contained Fe^{3+} ions in sufficient concentrations (Table 5) obtained as a result of the prior bacterial oxidation of Fe^{2+} to Fe^{3+} ions in the bioreactor using immobilized biomass of the iron-oxidizing bacteria *At. ferrooxidans* and *L. ferrooxidans*. These leach solutions contained also significant quantities of living bacteria of the species mentioned above (from approximately 4.10^7 cells/ml in solutions with 1 g/l Fe^{3+} ions to about 6.10^8 cell/ml in solutions containing 15 g/l Fe^{3+} ions). The role of bacteria in these short-term leaching experiments (with a duration of 120 hours) was not so essential because the solubilization of non-ferrous metals at the higher Fe^{3+} concentrations proceeded at high rates. However, in experiments of a long duration the role of bacteria to regenerate the Fe^{3+} ions was essential.

Table 5
Leaching of non-ferrous metals from the electronic scrap by means of ferric sulphate solutions generated as a result of the prior bacterial oxidation of Fe^{2+} to Fe^{3+} ions

Leach solution	Metals solubilized within 120 hours, %		
	Cu	Zn	Ni
Fe^{3+} (15 g/l) + *At. ferrooxidans*	97.0	97.4	98.1
Fe^{3+} (15 g/l) + *L. ferrooxidans*	97.2	98.1	99.0
Fe^{3+} (15 g/l) + mixed culture	98.9	99.2	99.7
Fe^{3+} (9 g/l) + *At. ferrooxidans*	95.2	95.0	96.1
Fe^{3+} (9 g/l) + *L. ferrooxidans*	95.0	94.1	97.0
Fe^{3+} (9 g/l) + mixed culture	96.4	97.0	98.4
Fe^{3+} (3 g/l) + *At. ferrooxidans*	71.4	84.2	91.4
Fe^{3+} (3 g/l) + *L. ferrooxidans*	70.0	86.0	93.8
Fe^{3+} (3 g/l) + mixed culture	71.2	88.2	93.8

The chemical leaching of non-ferrous metals by means of sterile ferric sulphate solutions was also efficient and resulted in similar extractions of non-ferrous metals. However, the leaching by means of sulphuric acid was not efficient at the temperatures maintained during the experiments (37 °C). On the other side, it is well known that the zero-valent forms at that non-ferrous metals are efficiently oxidized and solubilized under aerobic conditions and high temperatures (>80 °C) in leach solutions consisting of concentrated sulphuric acid.

The dissolved non-ferrous metals can be recovered from the pregnant solutions by means of solvent extraction and electrowining as well as by means of precipitation as the relevant sulphides.

The leaching of precious metals from the residues by means of the alkaline solutions containing thiosulphate and amino acids as complexing agents for these metals was also efficient (Fig. 1). 98.1% of the gold and 97.4% of the silver were solubilized within 72 hours.

The degree of extraction of the dissolved metals from the pregnant solutions by cementation with Zn^0 was higher than 98%. The products from the cementation unit were mixed gold-silver concentrates which contained also copper and zinc as valuable components. These non-ferrous metals can be solubilized by leaching with sulphuric acid at high temperatures in the presence of oxygen. Then the concentrates can be processed by the conventional procedure for obtaining pure gold and silver.

The consumption of reagents during the leaching and cementation amounted to 9.1 g ammonium thiosulphate, 0.35 g protein hydrolysate and 0.14 g metallic zinc per kg of ore.

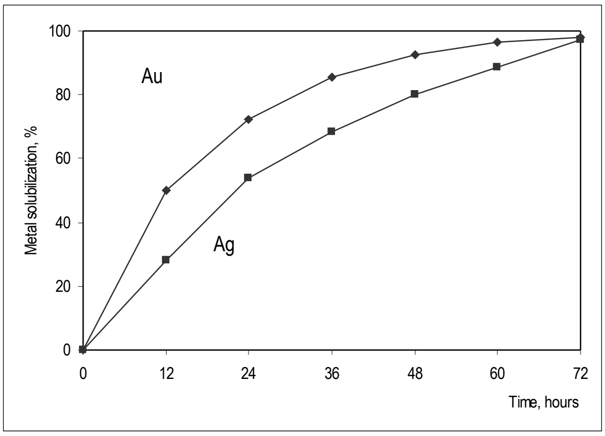

Fig. 1. Leaching of precious metals from the electronic scrap

The above mentioned results indicate that the combined biological and chemical leaching of non-ferrous and precious metals from electronic scrap can be regarded as an efficient method for extraction of these valuable components.

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