Polish J. of Environ. Stud. Vol. 16, No. 3 (2007), 447-451

Original Research

Investigation of Heavy Metals Leaching from Industrial Wastewater Sludge

K. Świerk[1], A. Bielicka[1], I. Bojanowska[1]* , Z. Maćkiewicz[2]

[1]Department of Environmental Engineering, Faculty of Chemistry, University of Gdańsk, Poland
[2]Department of Polypeptides Chemistry, Faculty of Chemistry,
University of Gdańsk, 18/19 J. Sobieskiego St., 80 – 852 Gdańsk, Poland

Received: January 26, 2006
Accepted: December 18, 2006

Abstract

Galvanic sewage sludge from electroplating plant was examined for leaching of heavy metals using various extracting solutions. The investigated parameters that influence heavy metals leaching were: contact time, type and concentration of leaching agents and form of sludge. The results of investigations show that the amounts of heavy metals (copper, nickel, chromium) released from industrial sludge using various leaching agents were from 0.07% to ~99% of their total contents. The form of sludge (air – dry or mineral residue) has a significant influence on quantities of metals leached.

Keywords: heavy metals, leaching, fractionation, galvanic sludge

Introduction

Metal plating has been identified as an environmentally risky industrial sector concerning the potential hazardous nature of its own waste streams. The dangerous character and eco-toxicity of industrial galvanic sludge is related to high concentrations of leachable metallic species, particularly the transition metals like chromium, nickel and copper.

The large increase of sludge originating from the waste water treatment process has resulted in significant disposal problems. This disposal attitude leads to serious disadvantages, as it contributes to a great build up of environmentally hazardous materials on the earth's crust. When huge quantities of industrial sludge are deposited for a long time, hazardous substances may be released in the landfill and may percolate through the soil layers and reach groundwater [1-5].

It is widely accepted that the impact of heavy metals on the environment cannot be assessed by measuring only the total concentration of individual metals. Proper evaluation of the effect of heavy metals on the natural environment is possible by knowing their chemical forms and bindings with soil, sediment, sludge or solid waste components. The chemical association of metals in sludge greatly influences their release into the environment. That is connected with a large number of physical (*e.g.*, particle size, temperature, mode of contact with water) and chemical (*e.g.*, pH, redox, sorption properties, complexing agents) parameters [2, 6-14].

The most abundant metallic species which are mainly leached from sludge coming from galvanic plants are nickel, chromium, copper, zinc and iron. From an economical point of view, nickel, zinc, chromium and copper are the most interesting metal values to recycle, but the toxicity allied to the high levels of chromium cannot be forgotten [3, 15-18].

The aim of our work was to study the leaching process of heavy metals from industrial galvanic sludge using various extractants and evaluate the quantity of heavy metals that could be released to the ecosystem.

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*Corresponding author; e-mail: bojirka@chem.univ.gda.pl

Methods and Materials

Physico-Chemical Characteristic of the Sludge

In experiments, dewatered galvanic sludge from an electroplating plant was used. It was air-dried and ground in mortar. The studied galvanic sludge contained 9% water, 22% dry weight of organic substances, and the total amount of heavy metals were 1.024±0.02 gCr/kg d.w., 2.035±0.05 gCu/kg d.w., 6.815±0.2 gNi/kg d.w.

Leaching Experiments

The leaching processes were performed with air-dry weight sludge samples (sludge dried at room temperature for 2 months) having diameter 0.1-0.5 mm and also with mineral residue samples (sludge burned at 550^0C). Leaching experiments were carried out at room temperature in closed, cylindrical tubes. Each sample was treated with deionized water (pH=6.8), a solution of nitrogen acid (0.02 M HNO_3 – pH=2; 1 M HNO_3 – pH=1; 8 M HNO_3 – pH=0), and sodium hydroxide (0.1 M NaOH – pH=13, 1 M NaOH – pH=14). The solution volume – 12.5 mL (L) to sludge mass – 0.25 g (S) ratio (L/S) was kept constant at 50:1.

The investigation was carried out over 12 months with intermittent agitation. The quantities of heavy metals in supernatants were determined by Atomic Absorption Spectroscopy (AAS 30 Carl Zeiss Jena Company). The contents of heavy metals were measured after various leaching times: 1 hour, 24 hours, 1 week, 1 month, 6 months, 12 months (Table 1).

Results

The mean values with standard deviation value of the heavy metals contents in particular extracts are presented in Table 1.

Analysis of heavy metals leaching from galvanic sludge has shown that the highest amount of copper, nickel and chromium was released using 1 M HNO_3 and 8 M HNO_3, in which cases the sludge samples were completely dissolved and the concentration of heavy metals were 2.035±0.05 gCu/kg d.w., 6.815±0.2 gNi/kg d.w., 1.015±0.01 gCr/kg d.w.

Table 1. Copper, nickel and chromium contents in particular extracts after various leaching times.

Leaching agents	0.1 M NaOH			1 M NaOH			H_2O			0.02 M HNO_3			1 M HNO_3			8 M HNO_3		
Leaching time	Air-dry samples [mg Me/kg d.w.]																	
	Cu	Ni	Cr	Cu	Ni	Cr	Cu	Ni	Cr	Cu	Ni	Cr	Cu	Ni	Cr	Cu	Ni	Cr
1 hour	~2.0 ±0.4	172 ±94	n.a.[1]	55 ±2	295 ±5	35 ±3	~2.0 ±0.4	231 ±105	n.a.[1]	~2.0 ±0.4	430 ±90	n.a.[1]	1426 ±26	4918 ±149	n.a.[1]	1622 ±28	5093 ±272	n.a.[1]
24 hours	59 ±3	230 ±36	n.a.[1]	93 ±4	332 ±66	78 ±3	~2.0 ±0.4	277 ±28	n.a.[1]	~2.0 ±0.4	449 ±15	n.a.[1]	1530 ±44	5055 ±79	n.a.[1]	1629 ±19	5200 ±45	n.a.[1]
1 week	67 ±9	276 ±20	n.a.[1]	137 ±27	357 ±35	n.a.[1]	~2.0 ±0.4	291 ±14	n.a.[1]	~2.0 ±0.4	495 ±45	n.a.[1]	1605 ±20	5119 ±73	n.a.[1]	1667 ±84	5569 ±42	n.a.[1]
1 month	73 ±28	339 ±126	n.a.[1]	234 ±40	378 ±90	n.a.[1]	~2.10 ±0.4	447 ±73	n.a.[1]	~2.0 ±0.4	590 ±46	n.a.[1]	1627 ±19	5383 ±129	n.a.[1]	1676 ±30	5647 ±44	n.a.[1]
6 months	103 ±14	378 ±20	n.a.[1]	251 ±9	504 ±136	n.a.[1]	~2.0 ±0.4	518 ±70	n.a.[1]	~2.0 ±0.4	906 ±38	n.a.[1]	1775 ±20	5509 ±155	n.a.[1]	1777 ±21	5851 ±130	n.a.[1]
12 months	101 ±19	392 ±89	n.a.[1]	246 ±15	463 ±60	n.a.[1]	~2.0 ±0.4	548 ±117	n.a.[1]	~2.0 ±0.4	915 ±167	n.a.[1]	1841 ±15	6603 ±220	n.a.[1]	1825 ±7	6779 ±279	n.a.[1]
	Mineral residue samples [mg Me/kg d.w.]																	
1 hour	~1.5 ±0.2	206 ±69	71 ±1	~1.5 ±0.2	252 ±75	523 ±2	~1.5 ±0.2	206 ±69	51 ±1	~1.5 ±0.2	161 ±63	112 ±2	384 ±16	517 ±49	132 ±3	602 ±9	1394 ±64	132 ±2
24 hours	~1.5 ±0.2	212 ±8	71 ±1	~1.5 ±0.2	331 ±42	536 ±6	~1.5 ±0.2	238 ±76	81 ±1	~1.5 ±0.2	286 ±6	112 ±2	503 ±19	2287 ±41	132 ±2	698 ±16	3018 ±37	617 ±14
1 week	~1.5 ±0.2	234 ±64	147 ±5	~1.5 ±0.2	343 ±9	531 ±2	~1.5 ±0.2	283 ±62	100 ±2	~1.5 ±0.2	346 ±13	263 ±4	1270 ±21	3089 ±93	364 ±4	1896 ±37	4835 ±251	1003 ±4
1 month	~1.5 ±0.2	295 ±12	186 ±6	~1.5 ±0.2	346 ±23	529 ±1	~1.5 ±0.2	327 ±9	132 ±2	32 ±1	387 ±43	263 ±2	1660 ±35	4837 ±48	912 ±9	1952 ±50	5721 ±220	1004 ±5
6 months	~1.5 ±0.2	572 ±23	221 ±5	~1.5 ±0.2	701 ±99	486 ±39	~1.5 ±0.2	700 ±16	162 ±2	34 ±1	859 ±62	242 ±3	1914 ±24	5821 ±203	973 ±2	1958 ±37	6114 ±216	1013 ±11
12 months	~1.5 ±0.2	535 ±165	304 ±4	~1.5 ±0.6	673 ±80	547 ±10	~1.5 ±0.2	654 ±140	162 ±1	30 ±1	754 ±72	260 ±4	2023 ±8	6489 ±289	983 ±6	2035 ±47	6815 ±246	1015 ±10

[1] n.a. – not analyzed, Me – Cu, Ni, Cr

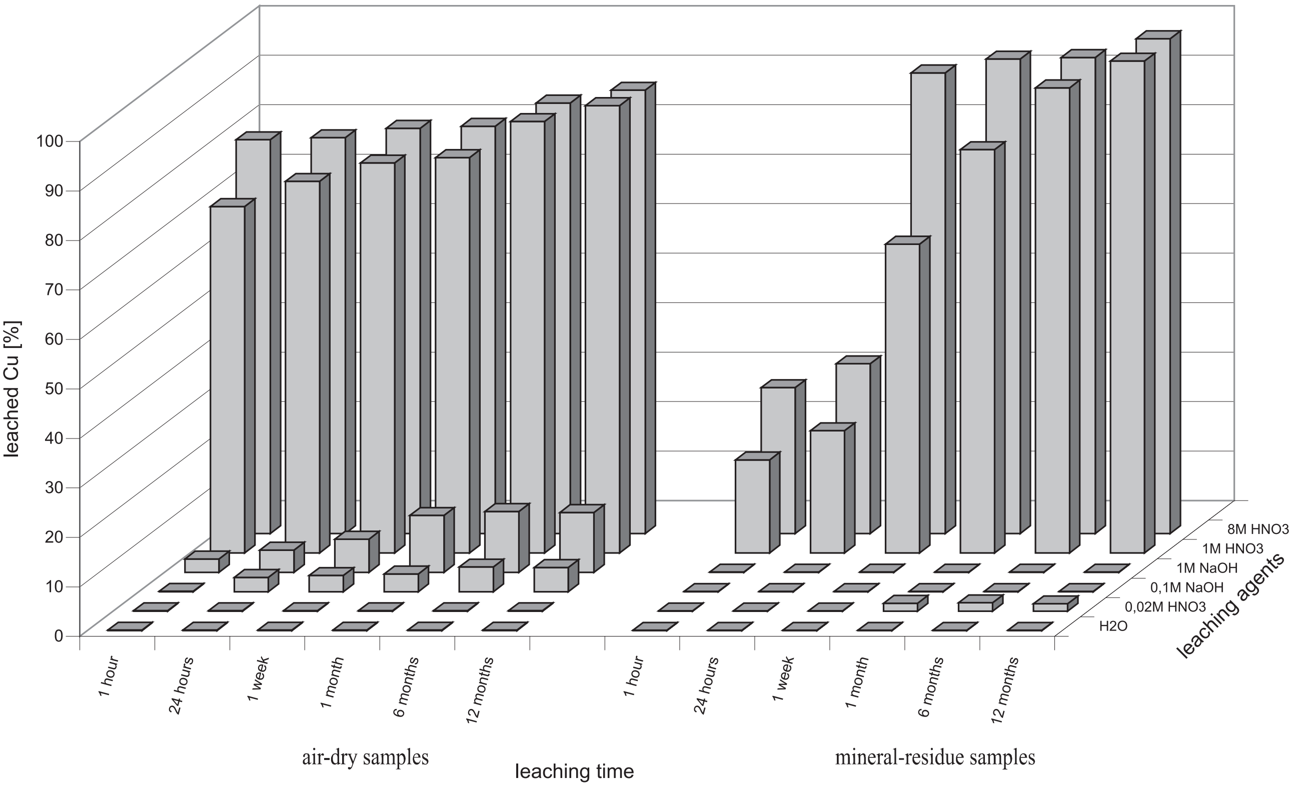

Fig. 1. Percent contribution of copper in particular extracts in the total copper content in studied sludge (L/S 50:1).

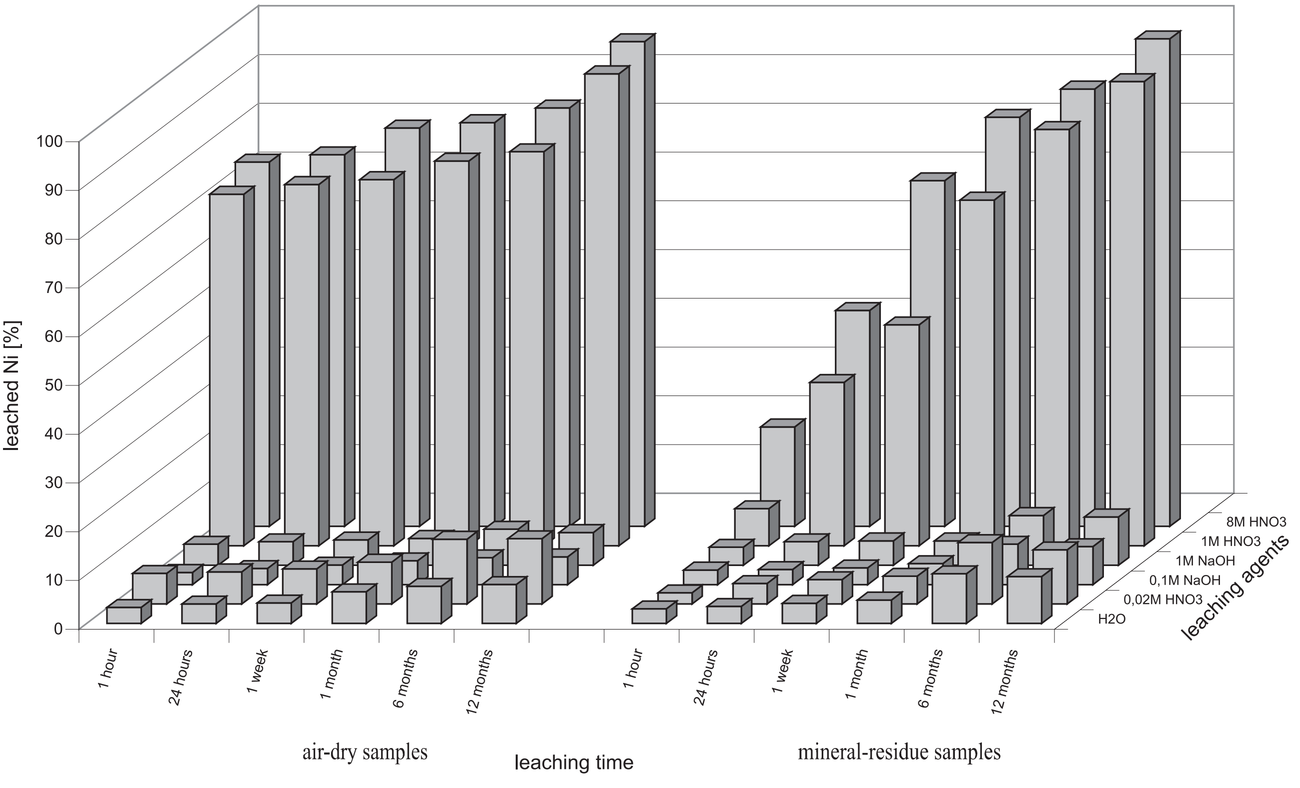

Fig. 2. Percent contribution of nickel in particular extracts in the total nickel content in studied sludge (L/S 50:1).

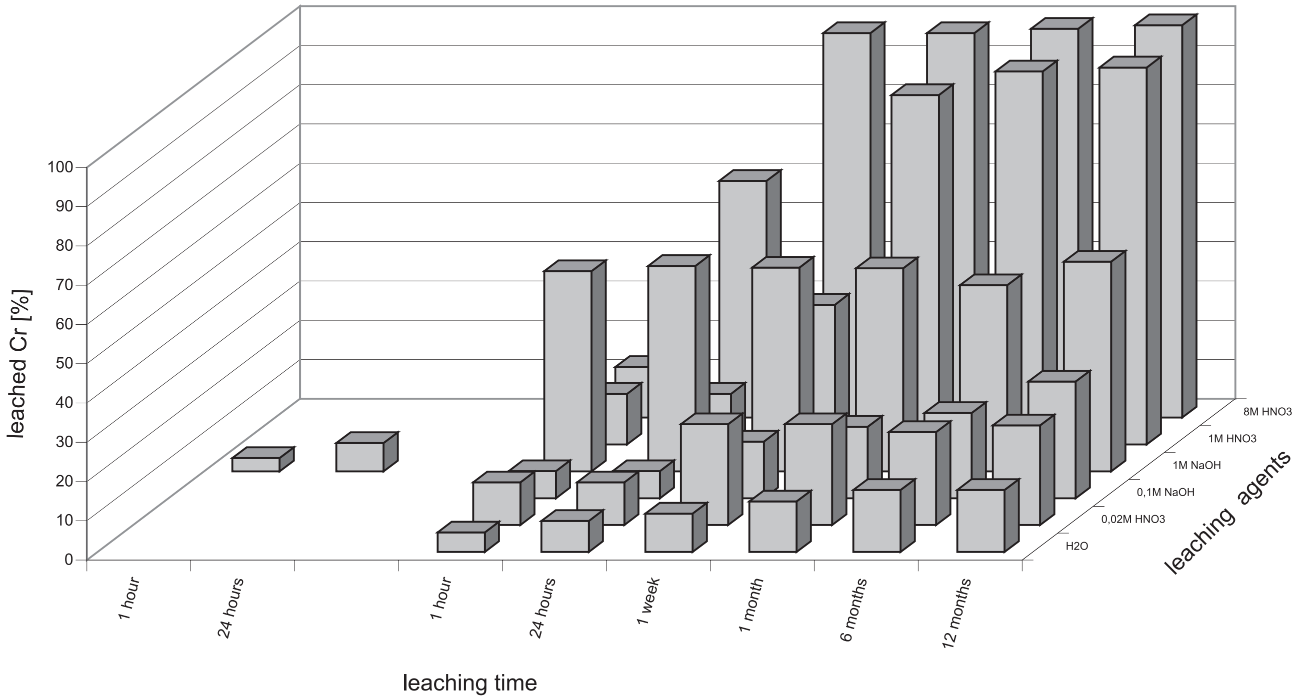

Fig. 3. Percent contribution of chromium in particular extracts of total chromium content in studied sludge (L/S 50:1).

The quantities of copper leaching from air-dry sludge samples using deionized water and 0.02 M HNO_3 were constant during the studied period of time (0.1%). The maximum values of percent contribution of copper in 0.1 M NaOH and 1 M NaOH extracts were 4.9% and 12.1%, accordingly (Fig. 1).

The copper amounts (0.07%) leached from mineral residue sludge samples during the time of experiment were constant when 0.1M NaOH, 1M NaOH and H_2O were used. For the 0.02M HNO_3 leaching the increase of copper content (from 0.07% to 1.6%) in extract after 1 month was observed and it was constant during the rest of the experiment (Fig. 1).

The amounts of nickel leaching from air-dry and mineral residue sludge samples using 0.1 M NaOH, 1M NaOH, H_2O and 0.02 M HNO_3 were increasing similarly during the studied period of time (Fig. 2). For 1 M HNO_3 and 8 M HNO_3 leaching the different contents of nickel from air-dry and mineral residue samples were determined. During 1 hour of leaching process using 8 M HNO_3 only 20.4% of Ni was released from mineral residue sample. On the contrary, it was 74.7% of Ni from air-dry sample (Fig. 2).

Results from chromium leaching showed that there was a significant difference in the amount of chromium released from air-dry samples and mineral residue samples (L/S 50:1). The process of sludge burning at 550°C had a major influence on chromium leaching.

The highest amount of chromium was released from mineral residue samples using 1 M HNO_3 and 8 M HNO_3 (Fig. 3). The chromium quantities leaching from sludge using 1 M NaOH were constant within the time of the experiment (52%).

The much smaller amount of chromium released from sludge was determined for 0.02 M HNO_3 (max. 26%) and H_2O (max. 16%) (Fig. 3).

Conclusions

The results obtained show that the amounts of copper, nickel and chromium released from industrial galvanic sludge using various leaching agents were from 0.07% to ~99% of total content. The form of the sludge (air-dry or mineral residue) had a great influence on quantities of metals leached. The highest amounts of metals were released from mineral residue samples using 1 M HNO_3 and 8 M HNO_3. For the 0.1M NaOH, 1M NaOH and H_2O leaching from mineral residue samples the quantities of copper were constant during the time of the experiment. On the contrary, the amounts of nickel leached from air-dry and mineral residue samples using the same extractants were similarly increasing. The chromium quantities leaching from air-dry sludge samples using 1 M NaOH after 24 hours were only 7% of its total content, whilst from mineral residue samples were about 52%. These results show that the huge part of chromium present in the sludge is bound with organic matter.

The results of study indicate that high amounts of heavy metals could be released into the environment from deposited industrial sludge. However, the more heavy metals present in galvanic sludge are released the higher the amount that can be recovered, so galvanic wastewater sludge could be not waste but raw material.

Acknowledgement

Financial support from the University of Gdańsk, project DS/8270-4-0093-6 and DS/8372-4-0183-6 is gratefully acknowledged.

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