The Recovery of Chromium from Galvanic Wastewater Sludge

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Abstract

The recovery of chromium from prepared (mixed and co-precipitated) sludge, generated during the neutralisation process of galvanic wastewater was investigated. Studied sludge contained hydroxide and oxide mixtures of various metals including chromium(III) hydroxide. The recovery procedure included precipitation of hydroxides and their dissolution, oxidation of chromium(III) to chromium(VI) and final extraction and reextraction of chromium(VI). The recovery of chromium from the mixed and co-precipitated sludge was limited by the sludge solubility in the sodium hydroxide solution. The yield of chromium recovery did not exceed 36%, which suggests that sludge should not be mixed after neutralisation [1, 2]. The recovery of chromium from the co-precipitated sludge was about 18% of its initial amount. This group of sludges should be managed according to the method proposed in papers [3, 4].

Introduction

Galvanic wastewater includes Cr(III), Cr(VI), Cu(II), Ni(II), Fe(III), Pb(II), Zn(II) and its neutralisation (after the previous detoxification) leads to the co-precipitation of the hydroxides and oxides, which after the process of dehydration are stored at a landfill [1] (in this paper they are referred to as **co-precipitated sludge).** Frequently, in spite of previous separation of the wastewater streams - into chromium and other streams, a separate neutralisation process using sodium or calcium hydroxide is applied; the sludge is mixed and stored in graveyards at the landfills (here referred to as **mixed sludge).** Both types of sludge are called **galvanic sludge.**

Materials and Methods

The studied processes were controlled by pH and chromium concentration measurements. The pH measurements were conducted using pHmeter (FIACH EC 20, 50075 model). Both chromium(VI) and chromium(III) concentrations were determined spectrophotometrically (HACH DR/2000) using HACH reagents, according to the application notes. The standard deviation of the analytical method for chromium(VI) was calculated to be ± 0.003 mg/dm^3 and for total chromium ± 0.025 mg/dm^3. Chromium(VI) was determined as a complex with 1,5-diphenylcarbohydrazide according to Polish norm PN-77/C-04604/08 and chromium(III) according to norm PN-77/C-04604/02. Chromium(VI) was also determined spectrophotometrically at wave length 400 nm in alkali solution of pH > 10. Total chromium and other cations concentration was measured using Atomic Absorption Spectroscopy Method (AAS system 30 - Karl Zeis Jena).

The chromium recovery process from all types of sludge was carried out according to the schematic diagram presented in [2]. The investigation included precipi-

tation of the sludge, its dissolution in 1M NaOH; oxidation of chromium(III) using 30% hydrogen peroxide at pH > 10 (**I stage**); extraction of chromium(VI) from investigated feeds using triisooctylamine in chloroform (the concentration of amine was 0.05M), acidification by sulfuric(VI) acid to pH=2. Chromium(VI) from the organic phase was reextracted to the 2M solution of sodium hydroxide (II **stage**).

In the tables the arithmetic mean of the obtained results, after each extraction step, was presented.

Obtained results have the following values of standard deviations: s_R=4.5% - mixed sludges, s_R=7% - co-precipitated sludges. The standard deviation (s_R) value was estimated according to the literature [5].

Results

Galvanic sludge (mixed and co-precipitated) obtained in the laboratory conditions were called: *fresh* (investigated after precipitation), *one-* and *four- week old* (their investigations were carried out after one or four weeks, respectively). The investigations allowed to specify the correlation between chromium recovery from the galvanic sludge and the age of this sludge.

Mixed sludge - metal hydroxides present in the galvanic wastewater were precipitated separately, then after draining, they were mixed in a homogeniser and treated according to the procedure proposed in [2].

Co-precipitated sludge - the hydroxides were precipitated from the solution containing cations of metals presented in galvanic wastewater (including chromium) and further treated.

The processes of the individual hydroxide precipitation as well as co-precipitation were carried out by 1M sodium hydroxide solution. The chromium concentration in the initial solution for the separate precipitation of hydroxides was 2.160 g/dm³; while for the co-precipitation it was 1.511 g/dm³. Concentrations of another metal cations were at the same level. Hydroxide sludge was precipitated from 10 cm³ of initial solutions where chromium contents were 21.60 and 15.11 mg in the precipitation and co-precipitation processes, respectively. In order to avoid the dissolution of the chromium(III) hydroxide (amphoteric compound) during the co-precipitation process, sodium hydroxide was added to reach pH level 9-9.5. The process was controlled by measuring chromium concentration in the supernatant (below 3% of the initial value, coprecipitation was considered to be completed). Under these conditions only 15% of nickel was removed from the solution. In order to achieve complete nickel reduction in the galvanising plants wastewater, precipitation of nickel sulfide [6] is carried out in the final stage of purification.

Dissolution of the Sludge

Mixed and co-precipitated sludges were dissolved in a 1M NaOH. Considering chemical properties of individual hydroxides, it was expected that chromium(III) and lead(II) hydroxides would dissolve and the others remained insoluble in alkali solutions. Obtained results for

Cu(II) and Ni(II) confirmed this assumption. Sodium hydroxide was used as a solvent for mixed and co-precipitated sludge (50-times stoichiometric excess). The process was conducted in different temperatures (25, 45, 60°C) and with different reaction time (24-120 hours). The increase of the temperature from 25°C to 45°C caused decrease of the chromium release from both types of sludge, up to 8-10%. It is likely that changes in the sludge structure led to a decrease in their solubility while increasing the temperature [6]. Prolongation of the solution time from 24 to 120 hours, at 25°C, did not significantly influence the process yield.

The release of chromium from the mixed sludge was at the level of 40%, regardless of sludge age. Lower chromium recovery (21%) was obtained from co-precipitated sludge. The age of sludge did not have a significant effect on the process yield (within the studied period of 4 weeks).

On the basis of the conducted study it was assumed that galvanic sludge (both types) is soluble in a 1M sodium hydroxide solution at 25°C. The time of solution was established to be 24h. The results of chromium(VI) recovery from mixed and co-precipitated sludge investigations are presented in Table 1.

Mixed Sludges

Table 1 presents the yield of chromium(III) release in the mixed sludge dissolution process.

Table 1. Yield of chromium(III) release from mixed sludge.

Sludge Age	Z_o [mg]	Z_r [mg]	W_r [%]
Fresh sludge	21.60	8.00	37.0
One-week old sludge	21.60	7.80	36.1
Four-week old sludge	21.60	7.62	35.3

where: Z_o - content of chromium(III) in the initial solution; Z_r - content of chromium(III) in the solution after the sludge dissolution; $W_r = (Z_r/Z_o) \times 100$ — chromium release from the sludge yield.

Oxidation of Chromium(III) to Chromium(VI)

Oxidation of Cr(III) into Cr(VI) using the 30% concentrated hydrogen peroxide, with its 45-times stoichiometric excess, was conducted in a heterophase system [2] as well as in the supernatant and the sludge.

The reaction mixture was shaken for 1 hour at 25°C. The H_2O_2 excess was removed by shaking the mixture for 1 hour at 70°C. Under these conditions 94% of chromium(III) present in the supernatant liquid was oxidized into Cr(VI), while in the heterophase system only 88% was oxidized. Increase of the oxidizing agent amount (to 80-times stoichiometric excess) did not influence the yield of the oxidation process. Part of the

Table 2. Comparison of the result of the recovery of chromium from the mixed sludge, which include processes: precipitation, dissolution of hydroxide mixtures and oxidation of Cr(III) into Cr(VI) ($Z_o = 21.6$ mg).

Sludge Age	Heterophase system			Homogeneous system		W_o [%]
	Z_r [mg]	$Z_{u/h}$ [mg]	W_r [%]	$Z_{u/c}$ [mg]	W'_r [%]	
Fresh sludge	8.00	6.99	87.3	7.40	92.5	33.3
One-week old sludge	7.80	6.80	87.1	7.05	90.4	32.1
Four week old sludge	7.62	7.02	92.1	7.32	96.1	33.2

where: Z_r - content of chromium(III) in the supernatant liquid after the sludge dissolution; $Z_{u/h}$ — content of chromium(VI) in the solution, in the heterophase system after the oxidation process; W_r $(W'_r) = (Z_{u/h \ (or \ u/c)} / Z_r)$ x 100 — oxidation process yield, calculated in relation to the initial content of chromium(III) in the supernatant liquid; $Z_{u/c}$ — content of chromium(VI) in the solution, after the chromium oxidation in the supernatant liquid; $W_o = (Z_{u/c} /Zo)$ x 100 — chromium recovery, calculated as a ratio of the chromium(VI) content in the solution after the oxidation (in the supernatant liquid) to the chromium(III) content in the initial solution, Zo - content of chromium(III) in the initial solution.

oxidizing agent was used in the oxidation process of Pb(II) into Pb(IV) (the presence of Pb(IV) was observed in the solution).

The yield of the first mixed sludge treatment stage, calculated as a ratio of chromium(VI) concentration in the solution obtained after the oxidation process to the chromium(III) concentration in the initial solution was 33%, regardless of sludge age. A very low yield of the chromium recovery process there was caused mainly by lack of complete dissolution of this sludge, which resulted in a low release of chromium(III). Table 2 presents the results of this stage of investigation.

Fig. 1. Content of chromium(VI) in the raffinate after successive extraction steps (mixed *fresh* sludge) in the extraction process of chromium(VI).

The Chromium(VI) Solvent Extraction from the Solutions Obtained after the Mixed Sludge Treatment

After the process of chromium(III) oxidation, the excess of hydrogen peroxide was removed from the solution by heating for one hour to 70°C. Investigated feeds were acidified with sulfuric(VI) acid to pH=2. This procedure was applied in the treatment of the chromic sludge [2].

Chromium(VI) was extracted from the investigated feeds using triisooctylamine in chloroform (concentration of TIOA=0.05M) as a solvent. Chromium(VI) was reextracted from the organic phase to 2M sodium hydroxide [7-9]. The extraction of chromium was conducted until the raffinate was colourless. Raffinate's pH was controlled after each step of extraction. Effective extraction of chromium(VI) ions occurs at pH=2. Table 3 presents chromium(VI) recovery from mixed sludge in the solvent extraction. Extraction processes of chromium(VI) from mixed *fresh, one-week* and *four - week old* sludge, expressed by ion content decrease in raffinate after successive extraction steps, are presented in the Figures 1 and 2.

In the further part of the sludge treatment, the frequency of chromium(VI) concentration control during the extraction and reextraction processes was reduced. Chromium(VI) extraction with the extractant recirculation and its reextraction into the same portion of sodium hydroxide were conducted. The chromium concentra-
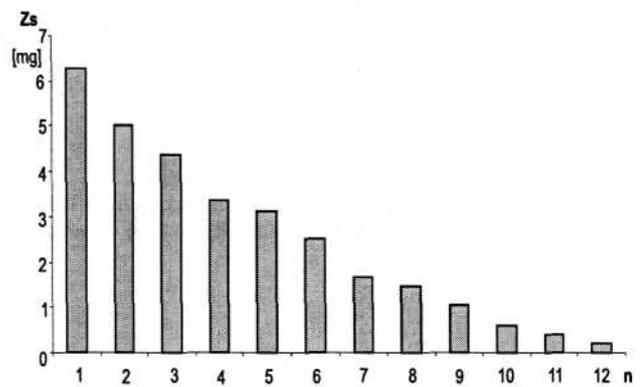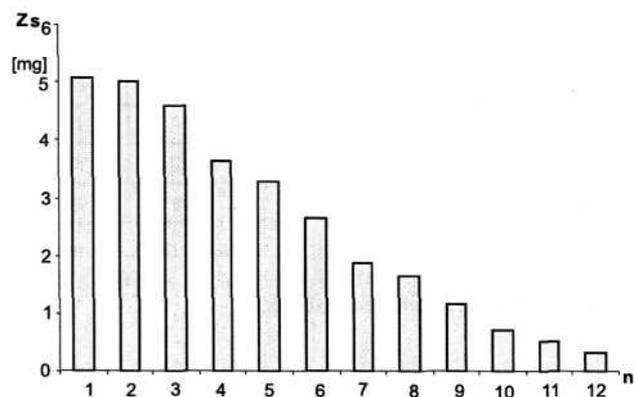

Fig. 2. Content of chromium(VI) in the raffinate after successive extraction steps (mixed *four- week old* sludge).in the extraction process of chromium(VI).

Table 3. Recovery of chromium(VI) from feeds obtained after the mixed sludges treatment in a solvent extraction and reextraction processes.

n	Fresh sludge $Z_{u/c} = 7.40$ mg			One-week old sludge $Z_{u/c} = 7.05$ mg			Four-week old sludge $Z_{u/c} = 7.32$ mg		
	Z_s [mg]	Z_e [mg]	W [%]	Z_s [mg]	Z_e [mg]	W [%]	Z_s [mg]	Z_e [mg]	W [%]
1	6.29	1.3		6.35	1.39		5.80	1.41	
2	5.02	0.93		5.12	0.96		5.00	0.99	
3	4.39	0.64		4.54	0.71		4.59	0.75	
4	3.34	0.62		3.57	0.70		3.64	0.73	
5	3.13	0.54		3.27	0.67		3.26	0.69	
6	2.50	0.42		2.78	0.49		2.62	0.45	
7	1.66	0.35	84.3	1.79	0.40	93.3	1.86	0.38	91.1
8	1.45	0.32		1.72	0.37		1.65	0.34	
9	1.04	0.31		1.25	0.27		1.14	0.29	
10	0.62	0.28		0.89	0.21		0.72	0.24	
11	0.41	0.25		0.56	0.16		0.51	0.19	
12	0.21	0.14		0.29	0.15		0.31	0.14	
13	–	0.10		–	0.10		–	0.10	
		Σ 6.24			Σ 6.60			Σ 6.73	

where: n - extraction step; $Z_{u/c}$ - content of chromium(VI) in the feed; Z_s - content of chromium(VI) in the raffinate; Z_c — content of chromium(VI) in the extract; $W = (\Sigma Z_e / Z_{u/c} \times 100)$ - extraction yield.

tions in feed and in reextract, after the process conclusion, were measured. Thanks to this method of process control some analytical errors have been eliminated. Chromium recovery yield was very high, which is presented in Table 4. Conducted investigations also confirmed the possibility of using the all media recirculation (extractant and reextractant).

Table 4. Chromium(VI) recovery yield from feeds obtained after the mixed sludges treatment in the solvent extraction with the extractant and reextractant recirculation.

Sludge age	Z_s [mg]	Z_e [mg]	W [%]
Fresh sludge	7.40	7.34	99.2
One-week old sludge	7.02	6.90	98.3
Four-week old sludge	7.32	7.29	99.6

where: Z_s - content of chromium(VI) in the feed; Z_e - content of chromium(VI) in the reextract; $W = Z_e/Z_s \times 100$ - yield of chromium extraction and reextraction.

It can be seen that sludge age does not have significant influence on the chromium recovery which is low and does not exceed 36% (Table 5).

Table 5. The total chromium recovery (after the I and II investigation stages) from the mixed sludge depending on their age.

Sludge age	Z_o [mg]	Z_e [mg]	W_0 [%]
Fresh sludge	21.60	7.34	31.67
One-week old sludge	21.60	6.90	35.09
Four-week old sludge	21.60	7.29	36.02

where: Z_o - content of chromium(III) in the initial solution; Z_e - content of chromium(VI) in the reextract; $W_o = Z_e/Z_o \times 100$ - the total chromium recovery yield from mixed sludges.

Table 6. Yield of chromium release from co-precipitated sludge.

Sludge age	Z_o [mg]	Z_r [mg]	W_r [%]
Fresh sludge	15.11	3.16	20.9
One-week old sludge	15.11	2.86	18.9
Four-week old sludge	15.11	2.62	17.3

where: Z_o - content of chromium(III) in the initial solution; Z_r - content of chromium(III) in the solution obtained after the sludges dissolution; $W_r = Z_r/Z_o \times 100$ - chromium release from the sludge yield.

Results of the chromium recovery investigations from mixed sludge clearly indicate that isolation and separate neutralization of galvanic wastewater streams should be carried out. Chromium sludge (consisting mostly of chromium(III) hydroxide) should be treated in accordance with the proposed procedure, leading to efficient chromium recovery, which has already been reported by the others [3, 4].

Co-Precipitated Sludge

During the dissolution of co-precipitated sludge in 1M sodium hydroxide (50-times stoichiometric excess) at 25°C, only 17 to 21% of chromium was released.

The chromium release from this type of sludge by 8M nitric(V) acid was obtained. The process was conducted at 24 and 40°C, changing the shaking time from 30 minutes to 48 hours. Only 21% of the chromium present in the sludge was recovered at 24°C. Additionally it has been found that the increase of temperature results in a decrease of chromium release.

60% of chromium recovery was obtained using 8M sodium hydroxide. Using 8M sodium hydroxide would require a large amount of sulfuric(VI), which acid had to be used in order to acidify feed in extraction process.

Oxidation of the released chromium(III), present in the supernatant was carried out using hydrogen peroxide in the alkaline solution (conditions adopted for mixed sludge). Efficiency of 90% was attained.

Chromium(VI) extraction and reextraction were conducted with the recirculation of the extractant and reextractant. The obtained yield of the extraction process was 95-97%.

Total chromium recovery from the co-precipitated sludge, calculated in relation, to the chromium content in the initial solution, was 18%. The low efficiency of chromium release during the sludge dissolution had a significant influence on the final result.

Conclusions

The presented work showed that galvanic wastewater streams should be isolated from other types of wastewater and neutralised separately. Obtained results also show that the above-described method is not sufficiently effective in chromium recovery from this sludge. They should be managed in accordance with the methods described in [3, 10-16], or alternatively, by investigation of other effective methods of sludge utilisation.

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