

Recovery of Chromium from Sludge Formed after Neutralisation of Chromic Wastewater

I. Bojanowska

Department of Environmental Engineering, Faculty of Chemistry, University of Gdańsk, 18 J. Sobieskiego St., 80-952 Gdańsk, Poland

Received: April 17, 2001

Accepted: November 26, 2001

Abstract

This paper describes chromium recovery from sludge generated while neutralising chromic wastewater. Chromium(III) hydroxide is the main component of these sludges. The recovery method is based on the transformation of chromium(III) hydroxide to chromium(VI) and was developed in our department. The method includes precipitation of the chromium(III) hydroxide and its dissolution, oxidation of chromium(III) to chromium(VI), solvent extraction and reextraction of chromium(VI). The chromium recovery yield of each procedure stage was in the range of 92 to 99%. Overall chromium recovery yield was about 90%.

Keywords: chromium, chromium plant, chromium sludge, solvent extraction

Introduction

Environmental concentrations of chromium are known to increase due to industrial development [1-5]. Two ionic forms of chromium, Cr(III) and Cr(VI) are present in various forms, both in soil, water and in the biota [6-8]. Chromium and its compounds originate in the environment mainly from anthropogenic sources. Further, in plants, soil and in the surface waters chemical the equilibrium between chromium speciation forms can exist.

Due to environmental toxicity of chromium, mainly chromium(VI) [9-14], it is crucial to limit its further discharge into the environment [15-17].

In this paper solvent extraction of chromium(VI) from the sludge containing chromium(III) hydroxide was investigated.

Neutralisation of Chromium Wastewater

The aqueous solutions of NaOH, HCl, H₂SO₄, Cr(III) and Cr(VI), iron and other metal ions are the main components in chromium industry wastewater [2]. Acidity and significant concentration of chromium compounds in the wastewater makes chromium industry of high environmental concern.

Technology of chromium wastewater neutralisation is, in the most cases, based on detoxification of waste, which is done by reducing chromium(VI) to chromium(III) and then, using sodium or calcium hydroxide, insoluble chromium(III) hydroxide is precipitated. At the same time other metal hydroxides are precipitated and their amount strictly depends on the cations concentration in the wastewater. Dewatered sludges are stored at landfills in specially prepared graves [2, 5, 18].

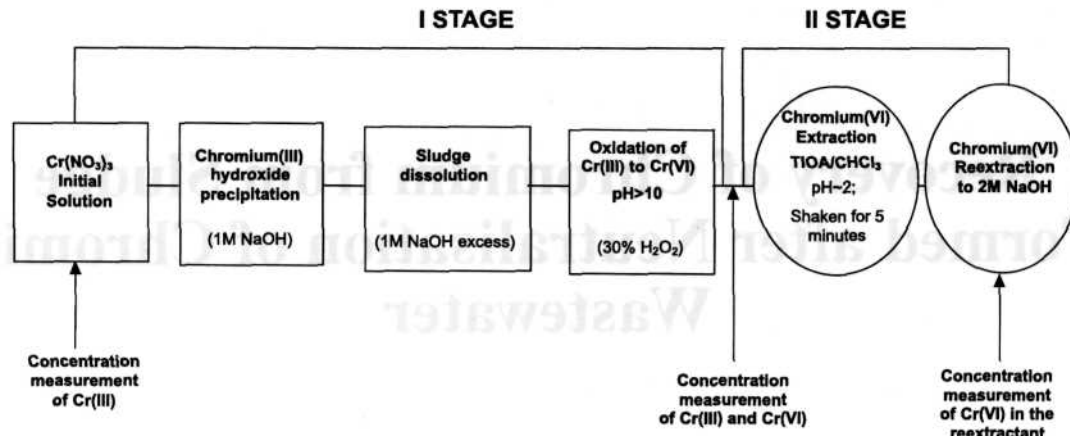


Fig. 1. Schematic diagram of the process recovery of chromium(VI) from chromium(III) hydroxide sludge.

Several methods of sludge management are proposed, for example utilising sludge as the additives to concrete and building materials. Chromium(III) hydroxide can also be used for pigment production [2, 19, 20].

The Recovery of Chromium as a Chromium(VI) from Chromium (III) Hydroxide

The sludge containing chromium(III) hydroxide was investigated after 3 different storage periods, enabling us to study solubility of hydroxide while ageing the sludge. The sludge was obtained in laboratory conditions and investigated as the fresh one (here and after called *fresh*), after one week (*one-week old*) and after four weeks (*four-week old*). The solubility of chromium(III) hydroxide strictly depends on the time of its storage, which is called "ageing of the sludge".

The chromium recovery process from chromium(III) hydroxide was run as specified in the diagram presented in Figure 1.

Investigation included two stages:

Stage I

- 1) chromium(III) hydroxide precipitation with 1M sodium hydroxide solution
- 2) sludge dissolution in 1M NaOH
- 3) oxidation of chromium(III) to chromium(VI) using 30% hydrogen peroxide solution at pH > 10

Stage II

- 1) solvent extraction of chromium(VI) ions from acidic aqueous solution (feed) using trioctylamine (TIOA) in chloroform (amine concentration $c_a = 0.05M$)
- 2) chromium(VI) reextraction from organic phase to 2M NaOH solution

Methods and Materials

The studied processes were controlled by pH and chromium concentration measurement. The pH measurements were conducted using pHmeter (HACH EC 20, 50075 model). Both chromium(VI) and chro-

mium(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 $\pm 0.003 \text{ mg/dm}^3$ and for total chromium $\pm 0.025 \text{ mg/dm}^3$. 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 the norm PN-77/C-04604/02. Chromium(VI) was analysed also spectrophotometrically at the wavelength 400 nm in alkali solution of pH > 10. Total chromium concentration was measured using Atomic Absorption Spectroscopy Method (AAS - system 30 - Karl Zeiss Jena).

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

Obtained results have the following value of standard deviation $s_R = 2.5\%$. The standard deviation (SR) value was estimated according to the literature [21].

Results

The processes of hydroxide precipitation were carried out by 1M sodium hydroxide solution. The initial concentration of chromium in aqueous solution equals 1.66 g/dm^3 . Chromium(III) hydroxide sludge was precipitated from 10 cm^3 of the initial solution, where chromium(III) content was 16.6 mg. In order to avoid dissolution of the chromium(III) hydroxide (amphoteric compound) the pH value of reactive mixture was maintained at the level of pH = 8-8.5. The precipitation process was controlled by measuring the chromium concentration in the supernatant. When the chromium concentration in the supernatant was below 2% of the initial value, the precipitation process was considered to be completed. For complete dissolution of the *fresh* chromium(III) hydroxide sludge, 2.5-time stoichiometric excess of 1M NaOH was used.

One-week and *four-week old* sludges were not completely dissolved in these conditions. Extension of the storage time to ca. 100 hours and 10-times stoichiometric excess of the sodium hydroxide led to complete *one-week* sludge dissolution. *Four-week old* sludge was still not dis-

Table 1. The solubility of the chromium(III) hydroxide at the function of the sludge age (2.5-times stoichiometric excess of 1M sodium hydroxide).

Sludge age	Z _o [mg]	Z _r [mg]	W _r [%]
Fresh sludge	16.60	16.25	97.9
One-week old sludge	16.60	14.05	84.6
Four-week old sludge	16.60	6.85	41.3

where: Z_o - content of chromium(III) in initial solution, Z_r - content of chromium(III) in the solution after sludge dissolution; W_r = (Z_r / Z_o) • 100 - dissolution efficiency of the chromium(III) hydroxide.

solved. This sludge was dissolved in 8M NaOH solution; however, such a high hydroxide concentration could not be used due to the usage of sulfuric(VI) acid in the next stage of an experiment.

The solubility of the chromium(III) hydroxide depends on the sludge age which is illustrated in Table 1.

Further treatment of the *one-week* and *four-week old* sludges was carried on in the heterophase system (without separation of undissolved sludge).

Oxidation of Chromium (III) to Chromium (VI)

Oxidation of chromium(III) to chromium(VI) using 30% hydrogen peroxide was conducted (50-times stoichiometric excess, room temperature). The mixture of extraction system was shaken for 15 minutes and then H₂O₂ excess was eliminated by thermal decomposition

Table 2. Results of the first-stage of the investigations including: precipitation, dissolution and oxidation of Cr(III) to Cr(VI).

Sludge age	Z _o [mg]	Z _r [mg]	Z _u [mg]	W _u [%]
Fresh sludge	16.60	16.25	15.35	92.5
One-week old sludge	16.60	14.05	15.46	93.1
Four-week old sludge	16.60	9.85	15.31	92.2

where: Z_o - content of chromium (III) in the initial solution, Z_r - content of chromium(III) in the solution after sludge dissolution; Z_u - content of chromium(VI) after oxidation, W_u = (Z_u / Z_o) • 100 - the yield of the first investigation stage.

for 30 minutes at a temperature of 60°C or for 10 minutes at 70°C. The chromium(III) and chromium(VI) concentration measurements made after reaction have shown almost complete oxidation of Cr(III) to Cr(VI) (92-96%).

The oxidation yield of Cr(III) to Cr(VI) (after fresh sludge dissolution), determined in relation to chromium(III) concentration in the solution after hydroxide dissolution, was 97-99% and calculated in relation to the initial solution, it was only 92-96%.

Analogical procedure of chromium(III) oxidation during *one-week* and *four-week old* sludge treatments, in spite of their incomplete dissolution, was used. The oxidation reaction was carried out in the heterophase system. During the oxidation process sludge was dissolved progressively.

Chromium reclamation and its further oxidation from previous chromium(III) hydroxide sludge was at the level of 92.5% (the yield of oxidation was determined in rela-

Table 3. Recovery of chromium(VI) from feeds formed during treatment of chromium(III) hydroxide sludge by solvent extraction and reextraction processes.

n	Fresh sludge			One-week old sludge			Four-week old sludge		
	Z _u = 15.35 mg			Z _u = 15.46 mg			Z _u = 15.31 mg		
	Z _s [mg]	Z _e [mg]	W [%]	Z _s [mg]	Z _e [mg]	W [%]	Z _s [mg]	Z _e [mg]	W [%]
1	10.84	4.22	98.9	11.40	4.00	95.9	9.69	3.99	96.4
2	7.76	3.81		7.15	3.99		5.95	3.80	
3	4.69	3.05		3.75	3.35		2.44	3.62	
4	2.48	1.92		1.79	1.99		0.83	1.60	
5	1.37	1.33		0.30	0.96		0.16	0.95	
6	0.46	0.73		0.15	0.41		0.08	0.56	
7	-	0.12		-	0.13		-	0.15	
		15.18		14.83		14.67			

where: n - extraction step; Z_u - content of chromium(VI) in the feed after the first stage (I); Z_s - content of chromium(VI) in the raffinate; Z_e - content of chromium(VI) in the reextract, W = (Σ Z_e / Z_u × 100) - the chromium recovery yield from sludge calculated in relation to chromium(III) content in solution after the first stage, *W = (Σ Z_e / Z_o × 100) - the chromium recovery yield from sludge calculated in relation to chromium(III) content in initial solution, Z_o - content of chromium(III) in the initial solution.

tion to chromium(III) content in the initial solution). The results of the first stage are presented in Table 2.

Solvent Extraction of Chromium (VI) by TIOA in Chloroform

As it is presented at Figure 1, extraction and reextraction processes of chromium(VI) are procedures considered as the second stage of chromium recovery (Fig. 1). Methodology of carrying both processes was analogous to the chromium recovery process from wastewater [22-24]. The aqueous and organic phases were in the ratio 1:0.4. The extraction system was shaken for 5 minutes. Solvent extraction of chromium(VI) from solution, further called feed, obtained after first sludge treatment stage (acidified to $\text{pH} = 2$), was carried out in a multi-step using TIOA in chloroform. After each extraction step pH of raffinate was controlled and kept at the level of 2 to 3.5 (by introducing concentrated sulfuric(VI) acid to avoid further dillution). After separation of the phases, chromium(VI) was reextracted from organic phase to 2M NaOH solution. In reextraction processes fresh portions of sodium hydroxide solution or recycled NaOH solution were used. Procedures were presented in papers [22-24].

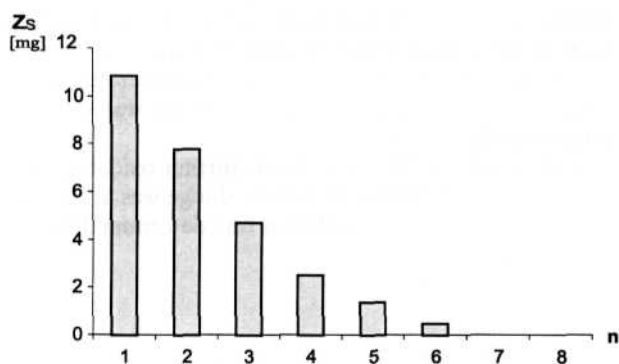


Fig. 2. Content of chromium(VI) in the raffinate after successive extraction steps (fresh sludge) in the extraction process of chromium(VI).

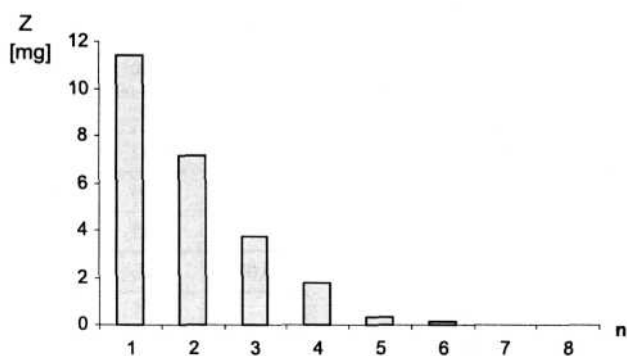


Fig. 3. Content of chromium(VI) in the raffinate after successive extraction steps (one-week old sludge) in the extraction process of chromium(VI).

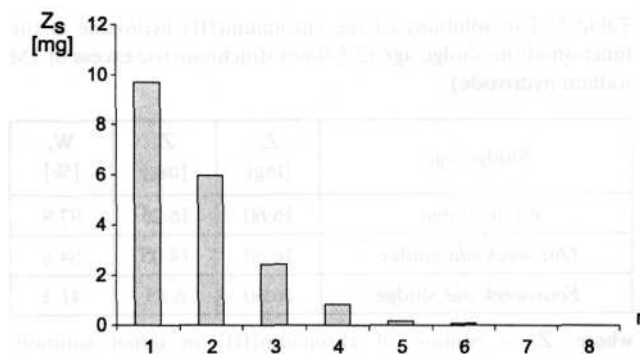


Fig. 4. Content of chromium(VI) in the raffinate after successive extraction steps (four-week old sludge) in the extraction process of chromium(VI).

After each extraction and reextraction step the measurements of chromium(VI) concentration in the raffinate and reextract were made. In Table 3 the extraction and reextraction of chromium(VI) yields from feeds are presented. Figs. 2-4 present extraction processes of chromium(VI) (expressed by decrease of ions content in raffinate after successive extraction steps) from all feeds.

The yield of chromium(VI) extraction from investigated feeds (estimated in relation to chromium content in the feed) was at the level of 96 to 99%. The yield of extraction was also calculated in relation to chromium(III) content in initial solution. This value was treated as a chromium recovery and was in the range of 88-92%.

Total chromium recovery from chromium(III) hydroxide sludge after I and II investigation stages (Fig. 1) was in the range of 88-92%. It is likely that obtained values may be lower than real ones, which may be affected by analytical errors committed at individual investigation stages, especially at the first one (hydroxide sludge precipitation, its dissolution and oxidation of chromium(III) to chromium(VI)). Extraction and reextraction processes yields were higher than 96% (Tab. 3).

Conclusions

Investigations clearly show that the age of sludge has no particular influence on total chromium recovery from chromium(III) hydroxide sludge (in the investigated time-period) (Tab. 3). During chromium oxidation process in the heterophase system *one-week* and *four-week old* sludge were dissolved progressively. The oxidation of Cr(III) to Cr(VI) yields were higher than 92% (Tab. 2).

Additionally, the proceeded studies show that chromium(VI) should be recovered directly from chromium wastewater or from sludge formed during its neutralization.

Acknowledgment

Financial support by the University of Gdansk, project DS/8270-4-0093-1 is gratefully acknowledged.

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