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Method for Decontamination of Toxic Aluminochrome Catalyst Sludge by Reduction of Hexavalent Chromium

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Abstract: The article is devoted to the neutralization of the harmful effects of aluminochrome catalyst sludge. Catalyst sludge is a waste product from petrochemical production and poses a serious threat to the environment and humans because of the toxic hexavalent chromium it contains. The emissions of Russian petrochemical enterprises' alumochrome sludge is 10,000–12,000 tons per year. In this paper, research related to the possibility of reducing the harmful effects of sludge by converting hexavalent chromium to a less dangerous trivalent state is presented. The reduction of hexavalent chromium was carried out with different reagents: Na_2SO_3, $FeSO_4$, $Na_2S_2O_3$, and $Na_2S_2O_5$. Then, a comparative analysis was carried out, and sodium metabisulfite was chosen as the most preferred reagent. The peculiarity of the reducing method was carrying out the reaction in a neutral medium, pH = 7.0. The reduction was carried out in the temperature range of 60–85 °C and under standard conditions. The maximum recovery efficiency of chromium from the catalyst sludge (100%) was achieved at 85 °C and 10 min. This method did not involve the use of concentrated sulfuric acid, as in a number of common techniques, or additional reagents for the precipitation of chromium in the form of hydroxide.

Keywords: catalyst sludge; hexavalent chromium; reduction; neutralization; deposition

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1. Introduction

Alumochrome catalyst is used in the petrochemical industry, in the process of the dehydrogenation of lower paraffins to C3–C5 olefins, which are used in the production of synthetic rubbers, plastic masses, and high-active additives for fuels [1–3]. The total volume of olefins produced by dehydrogenation methods in Russia is 600,000–700,000 tons per year [4].

The catalyst is an Al_2O_3-Cr_2O_3-SiO_2 system obtained by the thermal activation of gibbsite [5]. Russian companies use catalysts of IM-2201 and KDM grades. The catalyst undergoes irreversible deactivation due to changes in the state of the active component, as well as being destroyed by mechanical action. The catalyst fragments are carried out of the reactor zone in the form of dust, which makes it necessary to carry out wet scrubber cleaning [6,7]. As a result, watered-down catalyst sludge, which the U.S. Environmental Protection Agency (EPA) classifies as a Group A carcinogen for humans, is removed from the plant's reaction zone [8].

This sludge poses a serious threat because it contains trivalent and hexavalent chromium ions. The most stable oxidation degrees of chromium are trivalent and hexavalent. Hexavalent chromium is soluble in water in the entire pH range, while trivalent chromium can be dissolved or precipitated as chromium hydroxide in mildly acidic and alkaline environments of pH 4–8 [8]. Cr(VI) is the strongest carcinogen and mutagen; it is about 1000 times more toxic than Cr(III) [9,10]. Chromium is considered one of the top 20 pollutants on Superfund's list of priority hazardous substances over the past 15 years [11]. From this, we can conclude that all industrial waste containing hexavalent chromium must be thoroughly recycled.

Alumochrome catalyst sludge is not recycled and is stored in special landfills, which leads to the accumulation of large-scale hazardous waste [12–14]. The storage of highly toxic sludge is costly and creates environmental problems, such as the pollution of sewage, groundwater, and air space, and has a detrimental effect on the health of living organisms [15–17]. In this regard, the development of technology to reduce the toxicity of waste by removing hexavalent chromium, with subsequent recycling, is relevant [18,19].

Since the catalyst sludge has an initial pH = 7, the reduction of Cr(VI) to Cr(III) was carried out in a neutral medium rather than in a strongly acidic one, as previously used, which is a novelty. Moreover, sodium metabisulfite was used as a reducing agent, which was not previously used for the reduction of chromium. The method proposed in this work to recover hexavalent chromium from catalyst sludge can be used at petrochemical plants to reduce the environmental load.

2. Literature Review

To date, there are various methods for cleaning solutions of hexavalent chromium, such as extraction, sorption, and bacterial, and using inorganic and organic reducing agents. Over the past few years, methods of removing chromium from waste solutions from various industries have become increasingly diverse.

The extraction method for extracting hexavalent chromium from wastewater is discussed in an article by Ziwen Ying et al., which compared nine amide extractants with different alkyl groups and six diluents with different polarity [20].

Liping Dai and Anil Kumar considered liquid membranes as extractants [21,22]. Liu and Xiaoyun Wu et al. constructed a bipolar membrane electrodialysis system (BMES) for the simultaneous extraction of Cr(III) and Cr(VI) from chromium slurry in the form of Na_2CrO_4 [23,24].

Ion exchange is widely used for the wastewater treatment of Cr(VI) ions, and various types of resins, zeolites, and natural sorbents are used as sorbents. In a study by Zhenxiong Ye et al., a process combining ion exchange and reduction–deposition, based on pyridine resin SiPyR-N4 deposited on a silicon dioxide carrier, with a Cr (VI) removal efficiency of 99.3% from the solution [25], was proposed. Jiayu Lu et al. used a binary solution of sapind saponin and the surfactant cetyltrimethylammonium bromide to remove Cr (VI) and recorded 94% removal [26].

Biochar is used as an adsorbent to remove pollutants from industrial wastewater. Studies by Zixi Fan et al. and Jianhua Qu et al. investigated several types of activated and deactivated biochar to effectively remove Cr (VI) from polluted industrial wastewater [27,28]. For the adsorption of chromium from solutions in the works of Paulina Janik et al. and Changwoo Kim et al., graphene oxide was modified with various aminosilanes containing one, two, or three nitrogen atoms in the molecule [29,30]. In a study by Xufan Zhang et al., magnetic titanomagnegemite (Fe_2TiO_5) was sulfated with H_2S gas to increase the removal efficiency of Cr (VI) [31].

The electrochemical reduction (ECR) of Cr (VI) to Cr (III) was extensively described in the removal of Cr (VI) from contaminated water. In a research study, Fubing Yao et al. used a single-chamber cell with a titanium anode for the indirect reduction of Cr (VI) and the deposition of Cr (III) [32].

Electroflotation (EF) is effective for removing various types of organic and inorganic pollutants. A. V. Kolesnikov et al. studied the EF process in the removal of hydroxide Ni(II), Cr(III), and other metals from the solution, using sodium sulfate as the background electrolyte [33].

The use of nanomaterials, which are considered to be materials smaller than 100 nm, is gaining popularity. The use of some inorganic nanoparticles as reducing agents or catalysts can significantly increase the reduction rate of Cr (VI) [30]. In the works of Miroslav Brumovský et al. and Qianqian Shao et al., the exploitation of sulfidized iron nanoparticles to increase the reactivity and selectivity of nZVI, with respect to the target pollutant chromium [34,35], was considered. Some of the nanomaterials used were bifunctional MOF/titanate nanotube composites [36], chitosan-grafted graphene oxide (CS-GO) nanocomposite [37], and graphene/SiO_2 nanocomposites @polypyrrole [38].

Over the past few years, methods of removing chromium from solutions by biological waste from various industries have been gaining popularity. Living organisms such as bacteria, yeast, fungi, algae, and plants proved to be effective bioremediation agents. Biosorption is another phenomenon in which a product of biological origin and byproducts are used as an adsorbent, and the process of adsorption is called biosorption. In the works of Golovina V.V. and Bagauv A.I. [39,40], chromium was extracted from solutions by logging wastes, namely bark and sawdust. Cherdchoo W. et al. conducted studies on the adsorption of chromium on ground coffee and mixed tea waste [41]. Vilardi G. et al. studied adsorption on biomass from olive seeds [42]. Bacterial methods of chromium extraction were described in the works of Zorkina O.V. and Singh P. [43,44].

All of these methods have a number of drawbacks. Electrochemical processes are efficient but require a high energy supply and skilled labor. The adsorption process is also efficient, but, after several cycles, the material removal potential decreases. The bioremediation process is environmentally friendly, but it takes a long time to complete [44,45]. The choice of a suitable purification technology depends on the initial concentration of heavy metals, the operating costs, and the characteristics of the solutions containing chromium ions.

The reagent method (recovery method) is widespread because of the minimum cost and relative simplicity of its technological process, due to which the maximum extraction in a wide range of parameters of chromium-containing waste is provided [46]. The reduction of hexavalent chromium to trivalent chromium by inorganic reducing agents is carried out in an acidic environment, followed by the precipitation of metal ions in the form of hydroxides in an alkaline environment [47].

The most commonly used reagents to convert Cr (VI) to Cr (III) are the sodium salts of sulfuric acid: sulfite (Na_2SO_3), bisulfite ($NaHSO_3$), thiosulfate ($Na_2S_2O_5$), iron sulfate ($FeSO_4$), iron chips, and organic reducing agents. The reductions proceed according to the following reactions (1)–(4) [47–49]:

Reaction with sodium sulfite:

$$H_2Cr_2O_7 + 3Na_2SO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Na_2SO_4 + 4H_2O \quad (1)$$

Reaction with sodium thiosulfate:

$$H_2Cr_2O_7 + 2Na_2S_2O_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 2Na_2SO_4 + 2H_2O \quad (2)$$

Reaction with ferrous sulfate:

$$H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O \quad (3)$$

Reaction with iron shavings:

$$H_2Cr_2O_7 + 2Fe + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 7H_2O \quad (4)$$

The above reactions occur in the strongly acidic region, at pH = 2.5. Chromium is converted to the trivalent form as sulfate; the reagents used to precipitate the trivalent chromium as $Cr(OH)_3$ are $Ca(OH)_2$, Na_2CO_3, and NaOH. This reaction must be closely monitored, since chromium hydroxide completely dissolves when the pH is increased above 8–9 [8,48].

Such a purification scheme has a number of disadvantages, such as the use of concentrated sulfuric acid to acidify solutions and reagents for chromium precipitation in narrow pH ranges.

3. Results and Discussion

Alumina catalyst sludge, which was formed during isobutane dehydrogenation and is a green-colored slurry, was used as an object of study.

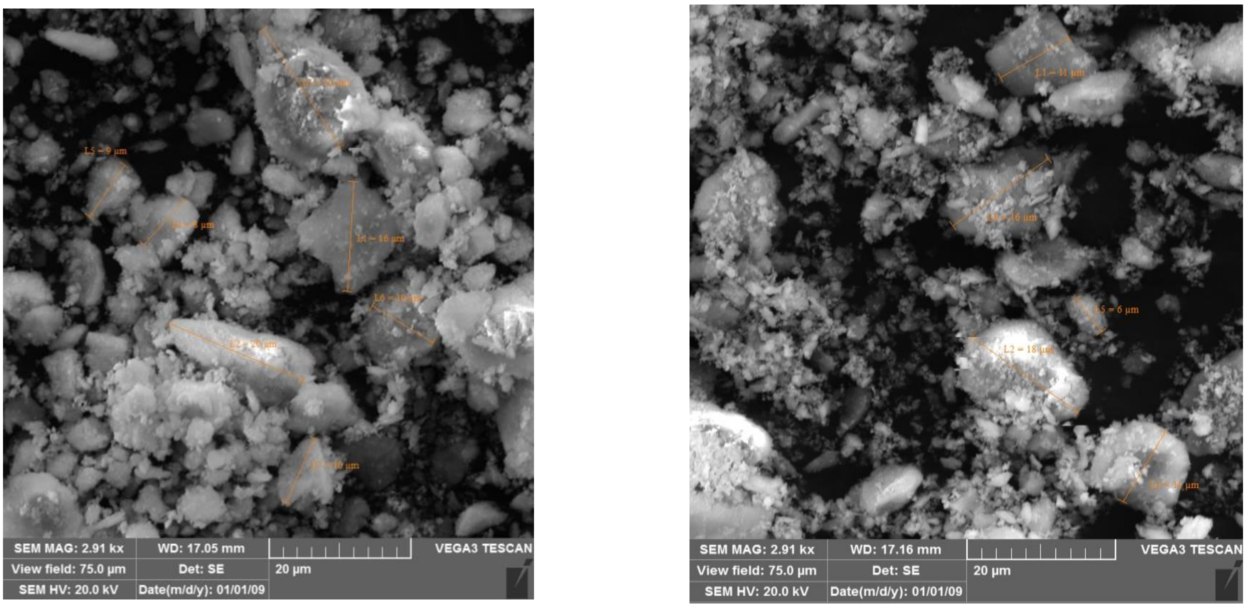
For analysis, the slurry had to be separated into liquid and solid phases, and their qualitative and quantitative compositions had to be determined. The filtration process was carried out using a vacuum.

The solid phase has a gray-green color, and the liquid phase has a bright yellow color (Figure 1).

Figure 1. Liquid and solid phases of catalyst slurry.

In the course of this research, it was revealed that trivalent chromium in the liquid phase of the catalyst sludge was absent, and no precipitate was formed when precipitating with a concentrated ammonia solution. The content of the hexavalent chromium in the solution is 1.2 g/dm^3.

The solid phase of the catalyst sludge is a finely dispersed powder with the presence of amorphous agglomerates ranging in size from 1 to 20 microns, as shown in Figure 2.



(**a**) (**b**)

Figure 2. SEM of the solid phase of the catalyst slurry: (**a**) before reduction; (**b**) after reduction.

The process of the reduction of hexavalent chromium with sodium metabisulfite in the pulp had no effect on the morphological structure of the solid phase.

The solid phase of the catalyst slurry is a finely dispersed powder with the presence of amorphous agglomerates ranging in size from 1 to 20 microns.

The results of diffractograms performed using X-ray powder diffraction are shown in Figure 3. According to X-ray diffraction analysis, we can see from the crystalline phases in the sample there is a mix of alpha aluminum oxide and delta aluminum oxide, as well as roughly dispersed crystallites of the solid solution Cr_2O_3-Al_2O_3 (chromaluminum oxide). According to X-ray analysis, we can say that there is a high proportion of the amorphous phase. The results of infrared spectrometry (ALPHA II, Bruker, Billerica, MA, USA) showed nothing but the presence of aluminum alpha-oxide (Figure 4).

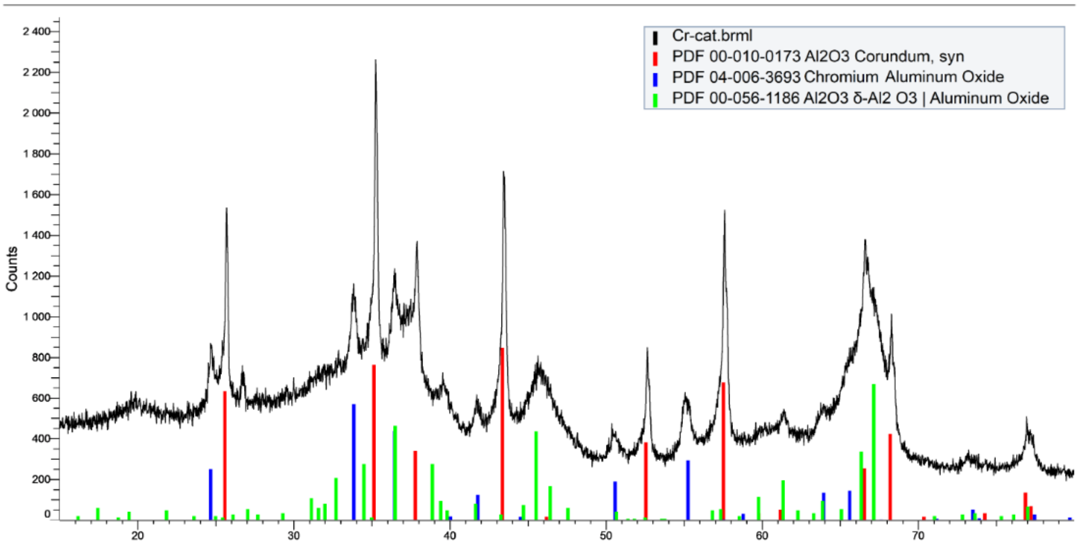


Figure 3. XRF of spent chromium catalyst.

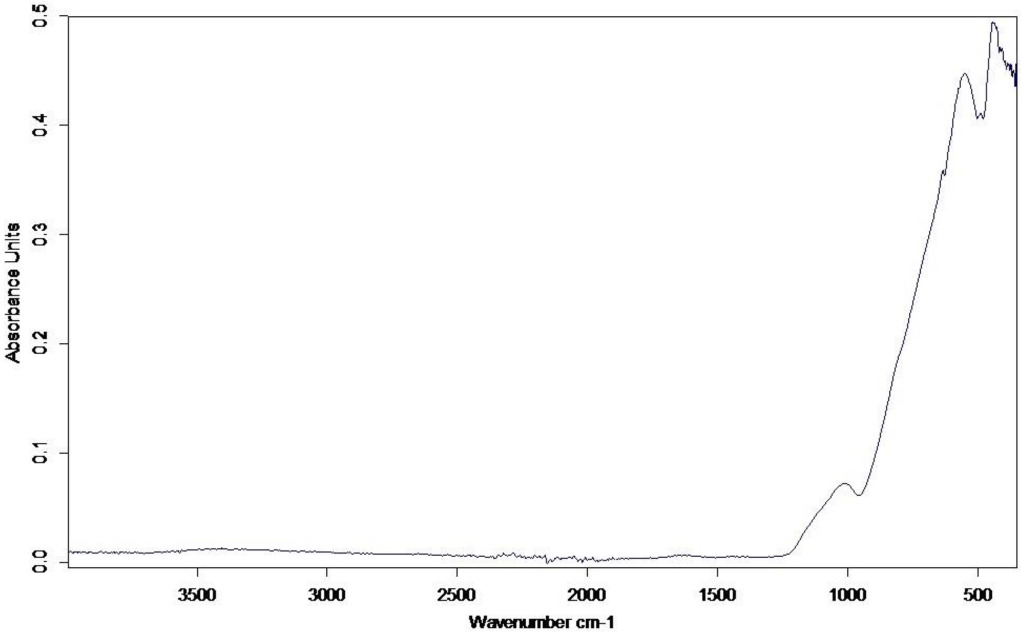


Figure 4. IR spectrum of the solid phase of catalyst sludge.

The composition of the solid phase of the catalyst slurry before and after the separation of water-soluble chromates is presented in Table 1.

Table 1. Chemical composition of the solid phase of catalyst sludge.

Name of Specimen and Research Instrument	Concentration, % wt.								
	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	ZnO	ZrO_2
Solid phase of catalyst sludge (initial) (Shimadzu)	72.46	11.61	2.49	0.18	0.23	11.74	0.21	0.01	0.23
Solid phase of catalyst sludge (initial) (ISP MS)	70.20	8.8	1.90	0.30	0.23	13.5	0.31	-	-
Solid phase of catalyst sludge (initial) (microanalysis: Tescan Vega 3)	71.8	10.08	2.94	0.35	-	13.6	0.27	-	-

Studies to identify the free chromates on the surface of the solid phase of the catalyst showed their absence.

The results showed that all trivalent chromium is contained in the solid phase and all hexavalent in the liquid phase, which means that only the liquid phase of the catalyst slurry is subjected to the reduction process.

3.1. Recovery of Hexavalent Chromium in the Liquid Phase of Catalyst Sludge

All experiments with the initial liquid phase of the catalyst slurry were performed without acidification with sulfuric acid for all the selected reducing agents. The reduction of hexavalent chromium was carried out in the temperature range of 50 °C–85 °C.

Hexavalent chromium in the liquid phase, at pH = 7, is in the form of chromates, as chromate ions prevail at pH > 6.5, according to the literature [50,51]. The conditions of the liquid-phase reduction process, and the results are shown in Table 1.

The interaction of chromates with sodium sulfite in a neutral medium follows the reaction (5).

$$2CrO_4{}^{2-} + 3Na_2SO_3 + 5H_2O \rightarrow 2Cr(OH)_3 + 3Na_2SO_4 + 4OH^- \quad (5)$$

The reaction produces a precipitate of amorphous chromium hydroxide with a gray-green color.

The quantity of sodium sulfite added to the liquid phase of the catalyst slurry was chosen based on earlier studies on model solutions. The mass ratio of sodium sulfite to the mass of the liquid phase of the catalyst slurry ranged from 0.0019 to 0.0060. Based on the literature data, sodium sulfite was added in excess, two or more times the calculated stoichiometric value [52,53]. In the practical implementation of the above interaction, it was found that the excess sodium sulfite remaining after the reaction was hydrolyzed, with a characteristic odor of sulfur sulfide (SO_2). The resulting mother liquor was highly alkaline, with pH = 11.7–12.5. Already with a recovery time of 30 min or more, the concentration of chromium ions in the liquid phase was less than 0.005 mg/L, which is less than the limit that the USEPA set for industrial wastewater discharges [8].

In order to reduce the formation of gas release and alkaline environment reduction, reactions were carried out with other reagents.

The interaction of hexavalent chromium with iron sulfate in a neutral medium follows the reaction (6).

$$CrO_4{}^{2-} + 3FeSO_4 + 4H_2O \rightarrow 2FeOHSO_4 + Cr(OH)_3 + Fe(OH)_3 + K_2SO_4 \quad (6)$$

Iron (III) hydroxide is a brown precipitate.

During the reduction with iron sulfate, in addition to chromium hydroxide, iron hydroxide precipitated out, which was an undesirable effect, since these precipitates must be separated later. Moreover, ferrous sulfate had worse chromium extraction results than sodium sulfite, so this reducing agent had to be abandoned.

Sodium thiosulfate showed a negative result when reducing Cr (VI) to Cr (III) in a neutral medium. The concentration of Cr (VI) in the solution in the temperature range of 50–75 °C did not change, so further studies with this reagent were discontinued.

In this series of experiments, it was assumed that reactions (7) and (8) proceed under these conditions under reduction. The reactions are presented in shrunken ionic form:

$$3S_2O_52^-{}_3 + 4CrO_42^- + 7H_2O \rightarrow 6SO_42^- + 4Cr(OH)_3 \downarrow + 2OH^- \quad (7)$$

$$3S_2O_52^-{}_3 + 2Cr_2O_72^- + 5H_2O \rightarrow 6SO_42^- + 3Cr(OH)_3 \downarrow + Cr^{3+} + OH^- \quad (8)$$

Since chromate ions predominate in a neutral medium [50,51], the Gibbs energy of reaction (7) was calculated under standard conditions, as follows: $\Delta_rG^0{}_{298} = -613.96$ kJ/mol. This indicates that this reaction is thermodynamically possible and runs spontaneously.

The application of sodium metabisulfite as a reductant of hexavalent chromium from the liquid phase of catalyst sludge in a neutral medium (pH = 7) leads to the transfer of up to 100% Cr (VI) to Cr (III), with the precipitation in the form of hydroxide, so this reagent was chosen for the reduction of chromium in the catalyst sludge pulp. Table 2 shows the conditions of the liquid-phase reduction process and the results of reduction.

Table 2. The conditions of the liquid-phase reduction process and the results.

Experiment Number	Ratio of the Reducing Agent's Mass to the Mass of the Liquid Phase of the Catalyst Slurry, g/g	Name of Reducing Agent	Process Temperature, °C	Process Time, min	Cr(VI) Removal Efficiency, %	Concentration of Cr^{+6} in the Liquid Phase before Reduction, g/L	Concentration of Cr^{+6} in the Liquid Phase after Recovery, g/L	pH of the Liquid Phase before Recovery	pH of the Liquid Phase after Recovery
Reduction with sodium sulfite (neutral medium)									
1	0.0060	Na_2SO_3	50	30	20	1.205	1.113	7	11.7–12.5
2			75		98		MeHee 0.005		
3			85		100		0		
4			50	60	68		0.390		
5			75		98		MeHee 0.005		
6			85		100		0		
7			50	120	78		0.265		
8			75		100		0		
9			85		100		0		
10	0.0037		50	60	7		1.105		
11			75		12		0.64		
12			85		46		0.65		
13	0.0019		75		10		0.89		
Recovery with ferrous sulfate (neutral medium)									
14	0.0060	$FeSO_4$	50	60	31.10	1.205	0.375	7	2.5–3.0
15			75		33.61		0.405		
16			85		30.29		0.365		
Recovery with sodium thiosulfate (neutral medium)									
17	0.0060	$Na_2S_2O_3$	50	60	No sludge	1.205	1.160	7	8.8
18			75				1.070		
19			85				1.085		
Reduction with sodium metabisulphite (neutral medium)									
20	0.0035	$Na_2S_2O_5$	50	60	47	1.205	0.64	7	8.8
21			85	65	52		0.58		
22			85	120	55		0.54		
23			50	420	57		0.52		
24	0.0070		50	15	0		1.20		
25			85	60	100		0		

During storage of the reduced liquid phase, we observed that the precipitation of chromium hydroxide continues with time, and the solution becomes lighter. In this connection, a series of experiments on the incubation of the liquid phase of the catalyst sludge in the presence of sodium metabisulfite at 20 °C and with periodic stirring every 12 h was carried out. The results of the analyses are presented in Table 3.

Table 3. Changes in the parameters of the liquid phase of the catalyst slurry when incubated in the presence of sodium metabisulfite at 20 °C.

Duration of Experiment, Days	Concentration of Total Chromium in the Liquid Phase, g/L
0	1.21
2	1.10
3	0.92
4	0.89
5	0.86

Under this condition of the experiment, on the second day, the concentration of the chromium in the liquid phase of the catalyst sludge dropped by 18%. During reduction, the sediment, which over time thickened and separated from the liquid phase, also precipitated. During the next 120 h, the precipitation sludge considerably slowed down.

3.2. Recovery of Hexavalent Chromium in Catalyst Slurry

In this part of the work, studies were conducted on the recovery of hexavalent chromium from the liquid phase of the catalyst slurry without separating the solid phase. In the course of this study, the optimum ratio of the reducing agent mass ($Na_2S_2O_5$) to the slurry mass, g/g = 0.005, was found. The results of the study of the reduction kinetics are shown in Figure 5.

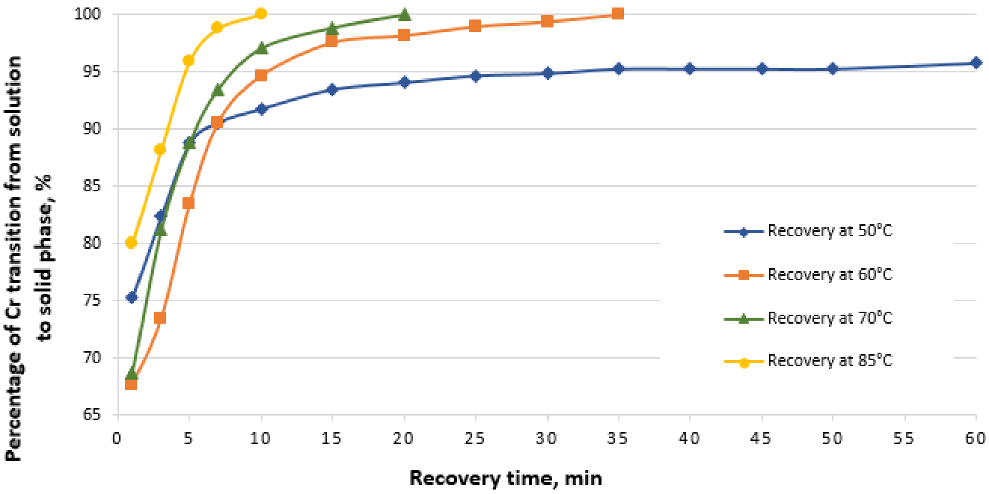


Figure 5. Kinetics of reduction of hexavalent chromium to trivalent chromium in catalyst slurry (ratio of reducing agent mass to slurry mass: g/g = 0.005).

Analysis of the mother liquor after pulp filtration showed that the recovery of hexavalent chromium from the catalyst slurry was possible at temperatures above 60 °C. At a temperature of 85 °C and a time of 10 min, the degree of conversion of chromium to the trivalent state reached 100%, which was more technologically optimal for the reduction process. The pH of the solution insignificantly increased and was 8.8.

Based on the results of the completed work, the following results can be summarized:

1. Sodium thiosulfate ($Na_2S_2O_3$) showed a negative result for the reduction of Cr (VI) to Cr (III) in a neutral medium. The concentration of Cr (VI) in the solution in the temperature range of 50–85 °C did not change.
2. Iron sulfate (anhydrous) in the reduction of Cr (VI) to Cr (III) in a neutral medium showed an average result, with an efficiency of about 30%. The reduction process proceeded without the use of additional precipitators, since the reduced chromium already precipitated out as $Cr(OH)_3$ in the process of reduction. Moreover, during the reduction with ferrous sulfate, in addition to chromium hydroxide, iron hydroxide precipitated out, which was an undesirable effect, since these precipitates must be separated later.
3. The reduction of Cr (VI) to Cr (III) in a neutral medium in the presence of sodium sulfite proceeded with 100% efficiency without the use of additional precipitators. However, during the reduction with sodium sulfite, the solutions acquired a strongly alkaline environment, which should be neutralized. In addition, this interaction produced a byproduct in the form of sulfur dioxide, which must be captured and disposed of.
4. The recovery of the liquid phase of the catalyst sludge with sodium metabisulfite ($Na_2S_2O_5$) completely proceeded without the formation of byproducts, as with the other reagents previously described. Its effect in a neutral environment led to a conversion of up to 100% of hexavalent chromium to the trivalent state, with the formation of a precipitate in the form of chromium hydroxide, without the use of additional reagents. Therefore, sodium metabisulfite was chosen for the reduction of hexavalent chromium in the catalyst slurry.
5. The experiments on the conversion of hexavalent chromium to the trivalent state in the catalyst slurry showed that the reduction process in the presence of sodium metabisulfite $Na_2S_2O_5$ can be directly carried out without the separation of the solid and liquid phases. Complete reduction took place at 85 °C after 10 min of interaction with the reducing agent.

4. Materials and Methods

This study assumed the possibility of using the reaction of effective reduction of Cr (VI) to Cr (III) by reducing reagents Na_2SO_3, $FeSO_4$, $Na_2S_2O_3$, and $Na_2S_2O_5$ not only from the liquid phase but also from the slurry. After the reduction reactions, the resulting precipitate was separated by filtration. The mother liquor was analyzed using X-ray fluorescence spectroscopy and the solid phase using an electron microscope equipped with an energy-dispersive analyzer.

The stages of the study included:

- separation of the liquid phase of the slurry from the solid phase;
- analysis of the solid and liquid phases before reduction;
- slurry liquid-phase recovery;
- filtration of liquid phase after recovery;
- analysis of liquid phase after recovery;
- selection of the most effective reagent for recovery of the liquid phase (Na_2SO_3, $FeSO_4$, $Na_2S_2O_3$, and $Na_2S_2O_5$);
- pulp reduction carried out with the selected reagent;
- determination of the chemical composition of the chromium content in the liquid and solid phases.

4.1. Separation of the Liquid Phase of the Pulp

Separation from the solid was carried out by filtration with a polyester filter cloth under a vacuum of 100 kPa. After filtration, the solid phase was washed with distilled water and dried until all moisture was removed.

4.2. Analysis of the Obtained Phases

Qualitative and quantitative analyses of the mother liquor after filtration were performed on a Shimadzu EDX-7000 energy dispersive spectrometer [54].

When a sample is irradiated with X-rays, the atoms in the sample emit fluorescent X-rays. Atoms of each element emit their (characteristic) radiation, which has a wavelength and energy strictly defined for the element. By recording the spectrum, the qualitative elemental composition of the sample is determined. By measuring the intensity of radiation of different wavelengths or energies, a conclusion can be made about the quantitative content of each element.

The EDX-7000 works based on a thermoelectrically cooled silicon drift detector with a chromium detection limit of 1 ppm. Quantitative sample analysis was performed by the calibration curve method. For this purpose, serially diluted standard samples were analyzed, and a fluorescence intensity vs. chromium content curve was plotted, which was used to quantify the element in unknown samples.

To determine the content of trivalent chromium in the solution, we used the gravimetric method, which is based on precipitation of trivalent chromium present in the liquid phase with a concentrated solution of ammonia [52].

Determination of the chemical composition of the solid phase of catalyst sludge was carried out using X-ray fluorescence analysis. Determination of morphology of solid phase of catalyst sludge was carried out using scanning electron microscopy and using microanalysis on a Tescan Vega 3 device with enlarging voltage of 20 kV. X-ray structural analysis of the solid phase using powder X-ray diffraction on Bruker D2 PHASER and infrared spectrometry (ALPHA II, Bruker) was also carried out.

Free chromates on the surface of the liquid phase of the catalyst were determined by boiling the solid phase of the catalyst in distilled water for 15, 30, and 60 min, and then the resulting solution was analyzed by X-ray fluorescence.

4.3. Recovering the Liquid Phase of the Slurry

The initial ratio of the reducing agent to the liquid phase was chosen based on analysis of the literature data [53,55], and then our own experiments were conducted with a decrease and increase in the dosage of the reducing agent. All reduction reactions were performed in a closed reactor at a stirring speed of 300 rpm. The weight of the samples was 100 g. The reduction process was carried out in the temperature range of 50–85 °C for 15–60 min and at room temperature with an interaction time of up to several days. During the reactions, the solution was discolored and the reduced chromium precipitated as $Cr(OH)_3$ hydroxide, which was consistent with the literature data of this study. The dynamics of pH change before and after the reaction was carried out using a pH meter.

4.4. Phase Analysis after Recovery

The cooled solution was filtered under vacuum at 100 kPa. The liquid phase was analyzed for residual hexavalent chromium content using X-ray fluorescence spectroscopy on a Shimadzu device. The chemical composition of the liquid phase was studied on a Shimadzu spectrometer, and the morphology of the solid phase was studied on a Tescan Vega 3 electron microscope.

4.5. Conducting Pulp Recovery with the Selected Reagent

The pulp was reconstituted in a closed reactor at 300 rpm agitation. The mass of the samples was 500 g. The process was carried out in the temperature range of 50–85 °C. A pulse of 5 mL was taken at regular intervals and filtered. The chemical composition of the liquid phase was studied on a Shimadzu EDX-7000 spectrometer, and the morphology of the solid phase was studied on a Tescan Vega 3 electron microscope.

5. Conclusions

According to the results of this study, we can conclude that the reduction of hexavalent chromium to trivalent chromium is possible in a neutral environment, rather than in a strongly acidic environment, as suggested in previously published works. Of all the studied reagents, sodium metabisulfite showed the most effective reduction of chromium, and it can be used to precipitate chromium in the form of hydroxide, both from the liquid phase and as part of the pulp of the catalyst slurry.

The advantage of the hexavalent chromium reduction process in a neutral medium is the formation of a precipitate without the use of concentrated sulfuric acid and additional precipitant reagents. Moreover, this method allows for the refusal of equipment designed for aggressive environments, which significantly reduces the economic costs.

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