

Removal of hexavalent chromium from ferrochrome dust effluent by chemical precipitation method

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Abstract

The dust produced by the electric arc method in the ferrochrome factory contains high amounts of hexavalent chromium, which has a high solubility in water and causes high environmental pollution. The present research has proposed a new method for neutralization of hexavalent chromium present in ferrochrome dust in solution environment by using chemical precipitation method. After checking conventional and non-conventional additives for neutralization by co-precipitation method, Iron sulfate is added to the aforementioned wastewater before release into the environment as a reducing agent of hexavalent chromium to trivalent chromium. Next, calcium sulfate was used as a stable complex forming factor in the system to remove chromium. XRD and XRF analyzes were used to characterize the dust and UV-Visible to determine the amount of chromium removed from the wastewater. The results showed that for 100 g/l of dust dissolved in water, adding 30 g of iron sulfate in the first stage and 20 g of calcium sulfate in the second stage reduces the content of hexavalent chromium from high values to below 10 ppm. Easy, high speed, cheapness and availability of additives are the merits of this method.

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key words

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Co-precipitation

Iron sulfate

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1. Introduction

Hexavalent chromium is a stable state in aqueous environments and is generally produced in industrial processes such as electroplating, chemical production, electrical and electronic equipment, and catalytic processes [1]. The mentioned ion has very high solubility and permeability in surface water, soil and underground aquifers. Due to the toxicity of hexavalent chromium for biological cells in amounts greater than its permissible limit (about 0.05 mg/l for drinking water [2, 3] and 0.5 mg/l in wastewater [4].), the lack of its effective removal can cause serious damage to organs and the environment. Hexavalent chromium compounds are also carcinogenic and can lead to irreparable damage to eyes, skin and mucous tissues [5]. The limited water resources on the one hand and the growing need of industries to use strategic materials on the other hand have increased the concern of environmental pollution with heavy elements such as Cr^{6+} . Based on this, extensive studies have been conducted in the field of removing these pollutants and developing strict standards for their safe disposal in the environment. Among these methods, we can mention surface adsorption [6], membrane filtration [6, 7], ion exchange [6], electrochemical methods [8], photocatalytic processes [6, 9] biological methods [10, 11] and precipitation [12, 13]. Meanwhile, the deposition method is one of the most common methods of removing heavy elements from environmental sources due to its ease and relatively low cost [6, 12].

The mentioned process starts by adding suitable anion to the wastewater containing heavy ion and forming insoluble salt in water and finally ends with the filtration of sediments settled from the solution. Ferrochrome is one of the most common and widely used types of ferroalloy, which is used as a precursor in the production of stainless steels, heat-resistant steels, wear-resistant steels, and tool steels [14, 15]. One of the most common methods of producing high-carbon ferrochrome is the use of submerged electric arc furnaces, in which melting and reduction are performed simultaneously [14, 15]. Due to environmental restrictions, it is inevitable to use a dust collector in the mentioned process to prevent dust particles from entering the environment. The dust collector columns divide the dust resulting from the process into two categories: fine (less than 400 μm) and coarse (above 400 μm). Coarse dust has the same grade as chromite ore and after briquetting using glue in a cold press, it is charged again in the process, while the

fine-grained type (less than 400 μm) has a lower grade and cannot be economically recycled [14].

Relatively high volume of fine dust production, low grade, economic inefficiency for its recycling along with environmental obstacles are a serious challenge for ferrochrome production units with smelting and regeneration methods and have doubled the importance of dealing with and neutralizing it effectively. It is important to note that due to its high volume-to-surface ratio, dust releases high amounts of hexavalent chromium when exposed to moisture and has a very destructive effect on underground water sources. Studies show that until now iron sulfide [13], metal hydroxides such as hematite [16], goethite [16] and alumina [16] have been used as adsorbents by surface absorption method. Among the limitations of the above adsorbents, we can mention the ability to remove chromium in low concentrations in the primary solution (below 100 ppm) and their relatively high price to remove Cr^{6+} . In the case that the concentration of hexavalent chromium released in the solution is above 100 ppm, it is not possible to use surface absorption methods with these adsorbents to achieve high neutralization values, and the chemical precipitation method is a more effective method. Table 1 summarizes various literature that adsorb hexavalent chromium.

The current research is based on the use of co-precipitation method to neutralize and remove the hexavalent chromium present in the exhaust dusts of the furnace dust collector of the Joghtai ferrochrome complex located in Sabzevar city of Khorasan Razavi province in Iran. The basis of the work is the use of iron sulfate and calcium sulfate additives as cheap and available materials for the effective removal of Hexavalent chromium in wastewater. Based on this, the most important innovations of the present plan are: providing a simple and cheap method to neutralize chromium from the dust of the ferrochrome production process, the stability of the created compound in environmental conditions, the high speed of the neutralization process, and the possibility of using air blowing as a stirrer and oxidizer to accelerate primary leaching of chromium in dust.

2. Materials and methods

2.1. Chemicals

The exhaust dusts of the dust collector system of Joghtai Ferrochrome Complex Furnace (Sabzevar-Iran) were prepared and transferred to the



Table 1: Comparison of effective doses of hexavalent chromium adsorbents

Absorbent agent	Absorbent amount (g)	Initial Cr concentration (mg/l)	Adsorption efficiency (%)	Ref.
Pyrite	20	100	100	[13]
Hematite	0.2	0.5	92	[16]
Goethite	0.2	0.5	94	[16]
Alumina	0.2	0.5	90	[16]

laboratory for the next steps. Iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), calcium sulfate (CaSO_4), sulfuric acid (H_2SO_4), Sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and hydrated lime or calcium hydroxide ($\text{Ca}(\text{OH})_2$) in industrial grade used through the neutral process.

2.2. Identification of phases and chemical composition

To check the physical and chemical properties of the used dust, introduction samples were prepared and investigated using analysis and X-ray fluorescence spectroscopy (ARL Advant XP device made in the United States) and XRD patterns were recorded by X'Pert Pro MPD at 40 kV and 30 mA with Cu-Kalpha radiation (wavelength = $1.54 \text{ \AA}$), the scanning speed of 0.02/s. Also, in order to read the amount of chromium in the solution, a UV-Visible spectrophotometer (Scan Drop, Analytic Jena Co, Germany).

2.3. Studying the release of chromium from dust in contact with water

One of the important issues in the neutralization process is the release of hexavalent chromium from ferrochrome dust in the water environment. For this purpose, in order to investigate and optimize the effect of time on the solubility of hexavalent chromium, first a solution containing 10 g of ferrochrome dust and 100 ml of water was prepared and at times of 3, 5, 7, 10, 13, 20, 45, 120 min and 24 h, sampling was done to be investigated.

2.4. Neutralization process

First, a 10 % pulp containing 10 g of dust and 100 ml of water was prepared. After complete release of hexavalent chromium from the dust (15 min), different amounts of additives (iron sulfate and calcium sulfate) were added to the pulp in two stages. In the first step, 3 g of iron sulfate was added to the pulp and stirred for 5 min. In the second step, 2 g of calcium sulfate was added to it

and the stirring continued for another 5 min. After each experiment, the neutralized pulp was filtered in 4 steps with Whatman 400 μm paper to make the solution free of any turbidity and ready for UV-visible analysis. In the required cases, the precipitate was neutralized, dried in an oven or in the open air, and dissolved in water again, and its behavior was investigated. To evaluate the stability of the neutralization operation, 0.5 M sulfuric acid solution was used instead of water to investigate the effect of the presence of acid on the reversal of the neutralization operation and the re-dissolution of hexavalent chromium. In order to increase the reliability of the results, the filtered pulp before and after neutralization was sent to the laboratory to perform the titration test.

3. Results and Discussion

3.1. Characterization of ferrochrome dust obtained from Sabzevar

ferrochrome complex dust collectors before and after neutralization. The amounts of elements in ferrochrome dust have been identified by XRF analysis, which is given in Table 2. According to the XRF analysis of the dust sample, it contained 8.8% chromium oxide, 26.6% magnesium oxide and 5.6% iron oxide. Also, the amounts of elements in neutralized dust are given in Table 3. X-Pert software was used to identify the dust-forming phases from mineralogical analysis by XRD method.

With the addition of iron sulfate and calcium sulfate for neutralization, the weight percentage of iron and calcium elements in the dust after neutralization has increased significantly. Other changes can be caused by different distribution of elements in the original dust sample, dissolution of compounds in water or removal from the system during filtering. By using the percentage of the constituent elements in the XRF test, the phases



Table 2: Chemical composition of ferrochrome dust based on XRF analysis

Compound	(wt. %)	Compound	(wt. %)	Compound	(wt. %)
Na ₂ O	9.6	Cl	6.1	SiO ₂	14.6
SO ₃	9.4	Fe ₂ O ₃	5.6	CaO	1.6
MnO ₂	0.2	Al ₂ O ₃	5.4	ZnO	1.2
PbO	0.1	K ₂ O	5.4	P ₂ O ₅	<0.01
MgO	26.1	NiO	0.1	TiO ₂	<0.01
Cr ₂ O ₃	8.8	La & Lu	<0.01	L.O.I	6.0

Table 3: Chemical composition of neutralized dust based on XRF analysis

Compound	(wt. %)	Compound	(wt. %)	Compound	(wt. %)
Na ₂ O	3.2	Cl	0.9	SiO ₂	8.0
SO ₃	9.7	Fe ₂ O ₃	23.9	CaO	10.9
MnO ₂	0.3	Al ₂ O ₃	2.9	ZnO	1.4
PbO	0.2	K ₂ O	2.0	P ₂ O ₅	0.2
MgO	12.3	NiO	0.1	TiO ₂	0.1
Cr ₂ O ₃	8.3	La & Lu	<0.01	L.O.I	15.8

proposed in the Xpert software were more limited, so that the element can have a high percentage in the material if it is mainly present in combination with other elements with a high percentage. Figure 1 shows the interpretation of the XRD diffraction pattern of ferrochrome dust. According to Figure 1 in the diffraction pattern before neutralization, chromium is present in dust in the form of potassium and sodium salts of chromate anion (CrO₄²⁻). Both of these compounds are yellow in color. Water also turns from colorless to yellow in contact with this dust.

As shown in the results of Section 3.3, no significant amount of neutralization could be achieved by adding iron sulfate alone, so it was assumed that some chromium was present in the post-neutralization dust in combination with calcium element. According to this possibility in the dust diffraction pattern after neutralization in Figure 1, chromium is proposed in the combination of two phases, the first in combination with iron and magnesium elements in the form of mineral donatite, and the second in combination with calcium and with the chemical formula Ca₁₀(CrO₄)₆(CO₃)

3.2. Effect of time on chromium release

Table 4 shows the effect of time on the release of chromium. The results show that with the passage of 15 min, the release has reached an almost constant point, and with the passage of time, the changes in hexavalent chromium concentration are very insignificant. So that you can add neutralizing additives to the solution after 15 min, the pH of which was measured between 7 and 8. Also, by repeating the experiment and adding a stirrer to one of the containers, the results show the positive effect of the stirrer on the release of hexavalent chromium from dust in water.

3.3. Neutralization operation

At first, with the assumption that with the increase of solution potential, the reduction process of hexavalent chromium to trivalent chromium will speed up, sulfuric acid, which has a high acid property, is added as the first addition to the solution containing 100 ml of water and 10 g of dust, which it has been stirred for 15 min, then stirred for 5 min. As the second additive and in order to

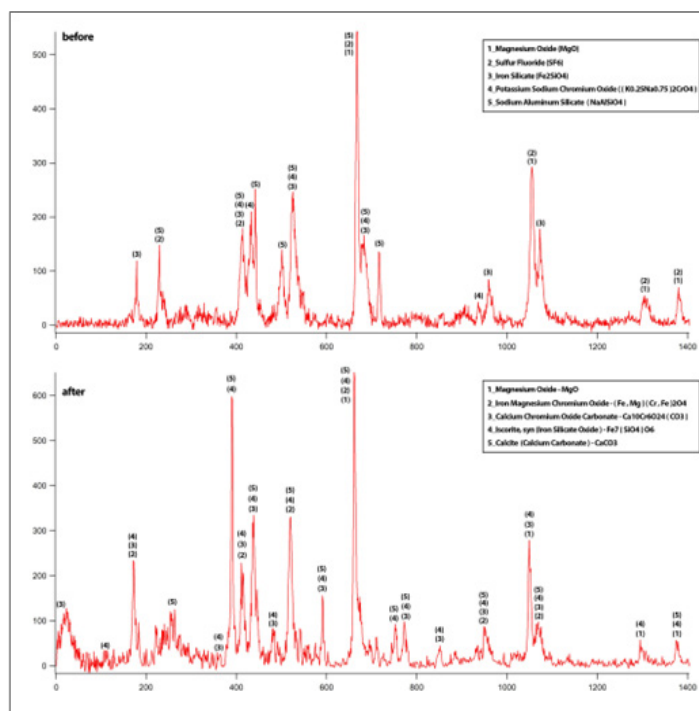


Figure 1: XRD diffraction pattern of ferrochrome dust before and after neutralization

Table 4: The effect of time on the dissolution rate of hexavalent chromium

Cr concentration (ppm)	Time (min)
4250	3
4500	5
4250	7
4750	10
6250	13
6362	20
6750	120
6862	24 (h)

remove chromium from the solution, sodium hydroxide, which has strong alkaline properties, was added to the solution and stirring was continued for 30 min, while the lid of the container containing the solution was covered with aluminum foil. In the next experiment, iron sulfate was added to the solution as an auxiliary substance to lower the potential of the solution, immediately after sulfuric acid and in the first step, and the rest of the process continued as before. Also, to investigate the effect of iron sulfate on chromium removal and to investigate the effect of lowering the potential, the previous experiment was repeated in the absence

of sulfuric acid. The results can be seen in Table 5.

The results show that additives in the first stage, if they are added alone to the solution, have a better performance in removing hexavalent chromium, and also the success rate of iron sulfate additive in removing chromium is higher than sulfuric acid. Increasing the amount of sodium hydroxide in the second stage also leads to a further reduction of hexavalent chromium at the end of the process. In order to investigate the effect of other salts on the neutralization process, sodium carbonate was replaced by sodium hydroxide in the next exper-



Table 5: The results of the neutralization process with the addition of sulfuric acid, iron sulfate and caustic soda

Test number	Dust (g)	Water (mL)	Time (min)	Sulfuric acid (drop)	Iron sulfate (g)	Covered	Sampling (h)	Cr ⁶⁺ concentration (ppm)
1	10	100	15-5-30	3	-	3	24	1520
2	10	100	15-5-10	1	1	2	0	2012
3	10	100	15-5-10	3	1	3	0	1756
4	10	100	15-5-10	-	2	2	0	1604
5	10	100	15-5-10	-	2	3	0	680

iments. All forms of sodium carbonate are white, water-soluble salts and produce moderately alkaline solutions in water. Due to the better performance in the removal of hexavalent chromium, iron sulfate alone was added in the first step and the rest of the test conditions were kept unchanged. The results are given in Table 6.

At first glance, the results prove that the performance of sodium carbonate in removing hexavalent chromium is better compared to sodium hydroxide, which was observed in Table 4. Also, increasing the amount of sodium carbonate, like sodium hydroxide in the previous experiment, improves the performance of the neutralization process, as can be seen in Table 6. By comparing the samples taken at the moment and after 24 h, it becomes clear that with the passage of time, the neutralization process with sodium carbonate is somewhat reversed.

The amount of hexavalent chromium remaining in the solution after neutralization with iron sulfate and sodium carbonate precipitates, even before the return of the neutralization process, is still far from the desired and safe level. For this purpose, in the next tests, hydrated lime additive, which is known

for its many applications in water and wastewater treatment, was replaced by sodium carbonate, and the rest of the test conditions were kept as before. The results are given in Table 7.

The results show that the combination of iron sulfate and hydrated lime in different doses has a good ability to remove hexavalent chromium from ferrochrome dust wastewater. There is one more step left for the finalization of additives to neutralize hexavalent chromium, and that is the reversibility test of the neutralization process. The neutralized samples with iron sulfate and hydrated lime additives did not have enough water for sampling after 24 h to read the amount of chromium, so the neutralized samples were dried in the open air for 48 h and dissolved again in 100 ml of water. After filtering, it was sent to the laboratory to read the amount of hexavalent chromium. The results can be seen in Table 8.

By examining the reversibility test results given in Table 8, it becomes clear that by re-dissolving the dust in water, the amount of hexavalent chromium has increased compared to the state when the sampling was done at the moment, and this means with the passage of time, a part of the neutraliza-

Table 6: The results of the neutralization process with iron sulfate and sodium carbonate additives

Test number	Dust (g)	Water (mL)	Time (min)	Sulfuric acid (drop)	Iron sulfate (g)	Covered	Sampling (h)	Cr (IV) concentration (ppm)
1	10	100	15-5-5	2	3	yes	0	550
2	10	100	15-5-5	2	3.5	yes	0	404
3	10	100	15-5-5	2	3	yes	24	1184
4	10	100	15-5-5	2	4	yes	24	996



Table 7: The results of the neutralization process with iron sulfate and hydrated lime additives

Test number	Dust (g)	Water (mL)	Time (min)	Iron sulfate (g)	Hydrated lime (g)	Covered	Sampling (h)	Cr (IV) concentration (ppm)
1	10	100	15-5-5	2	2	yes	0	0.658
2	10	100	15-5-5	2	3	yes	0	N.D
3	10	100	15-5-5	2	4	yes	0	0.156
4	10	100	15-5-5	3	3	yes	0	N.D

tion process of hexavalent chromium is reversed using iron sulfate and hydrated lime additives.

In search of a stable solution, the experiments were resumed by replacing calcium sulfate with calcium hydroxide (hydrated lime) and keeping the rest of the conditions constant. In Table 9, the amount of chromium removal immediately after adding calcium sulfate and after 60 min of neutralization are compared. The results show that the concentration of chromium remaining in the solu-

tion immediately after adding calcium sulfate is 37.5 ppm. Meanwhile, with the passage of 60 min, the neutralization process continued and hexavalent chromium was completely removed from the system.

In the following, the effect of reducing the dose of iron sulfate on the neutralization operation was investigated, and tests 3 to 5 in Table 9 are related to this issue. The results showed that by reducing the consumption of iron sulfate from 3

Table 8: Reversibility test results of the neutralization process with iron sulfate and hydrated lime additives

Test number	Dust (g)	Water (mL)	Time (min)	Iron sulfate (g)	Hydrated lime (g)	Covered	Sampling (h)	Cr (IV) concentration (ppm)
1	10	100	15-5-10	2	3	yes	48	11.1
2	10	100	15-5-10	2	4	yes	48	9.9
3	10	100	15-5-10	3	3	yes	48	4.2

Table 9: The results of the neutralization process with iron sulfate and calcium sulfate additives

Test number	Dust (g)	Water (ml)	Time (min)	Iron sulfate (g)	Calcium sulfate (g)	Sampling (h)	Cr (IV) concentration (ppm)
1	10	100	15-5-0	3	2	0	37.5
2	10	100	15-5-5	3	2	1	N.D
3	10	100	15-5-5	2	2	0	75
4	10	100	15-5-5	2	2	1	37
5	10	100	15-5-5	2	2	18	N.D
6	10	100	15-5-5	3	-	24	225



g to 2 g while keeping other operating conditions constant, the amount of chromium after neutralization reached 75 ppm and after 5 min it reached 37.5 ppm and then After 1 h, the same 37.5 ppm remained and after 18 h, the neutralization process was completed. Therefore, by reducing the use of sulfate from 3 g to 2 g, a longer time is required to remove hexavalent chromium from the solution. In test 6 from Table 9, the effect of removing cal-

age of chromium in the washed dust and the mass of the total dust, the amount of chromium was obtained and compared with before washing the dust. It was observed that after washing, the amount of chromium in the dust has decreased by about 180 mg, and assuming that all this amount of chromium is released by dissolving the dust in 100 ml of water, the amount of chromium in the solution reaches to 1800 mg/l or 1800 ppm. Therefore, the

Table 10: Titration test results of the solution before and after neutralization

Amount after neutralization (mg/l)	Amount before neutralization (mg/l)	Ion name
<0.1	380	Cr ⁺³
<0.1	1050	Cr ⁺⁶
<0.1	1430	Cr total

cium sulfate on the neutralization operation was investigated. As can be seen, without the presence of gypsum to complete the reaction and completely remove hexavalent chromium, some hexavalent chromium remains in the solution and high neutralization cannot be achieved with dry iron sulfate alone. In order to ensure the results, the pulp obtained from a process similar to test 2 of Table 9 was sent to the laboratory after filtering for titration test, the results of which can be seen in Table 10.

The large difference in the amount of chromium read in high amounts in the UV test and the titration test led to the formation of another test to validate the results of the tests. For this purpose, 10 g of ferrochrome dust was washed well by a filter press and the remaining dust was sent to the laboratory for XRF testing after drying in the oven and measuring the weight. The results can be seen in Table 11.

The weight of the dust after washing was measured to be 7.445 g. By having the weight percent-

results of UV tests in the upper range cannot be relied on, and the titration test results are correct in the upper range. On the other hand, considering that the basis of measurement in the titration method is the color of the solution, the UV test results are more reliable in low values.

Examining the results of Table 10 shows that the mentioned method, in addition to being effective in removing hexavalent chromium, also has a good performance in removing trivalent chromium. Also, the neutralized sediment resulting from test 2 of Table 9 was dried in an oven for 24 h at a temperature of 90 ° and was re-dissolved in water to check the reversibility of the neutralization process. Examining the results of dust re-dissolution in water showed that no hexavalent chromium remained in the neutralized sediment and its removal was done completely. In other words, after re-dissolving the neutralized sediment in water, no hexavalent chromium was released in water. The results of the neutralization reversibility test, in which a half molar solution of sulfuric acid was

Table 11: Chemical composition of washed ferrochrome dust based on XRF analysis

Compound	(wt. %)	Compound	(wt. %)	Compound	(wt. %)
Na ₂ O	3.4	Cl	0.9	SiO ₂	16.3
SO ₃	0.3	Fe ₂ O ₃	18.8	CaO	2.4
MnO ₂	0.6	Al ₂ O ₃	5.9	ZnO	2.8
PbO	0.1	K ₂ O	0.9	P ₂ O ₅	0.2
MgO	26.7	NiO	0.3	TiO ₂	0.1
Cr ₂ O ₃	13.2	La & Lu	<0.01	L.O.I	8.0



used instead of water, showed that all dissolved compounds with dust have the ability to co-precipitate effectively and stably with hexavalent chromium in a long period of time. As a result, even in the presence of acid, the passage of time cannot return the process of neutralization and release of hexavalent chromium.

An important point in guaranteeing the success of the mentioned method is adding iron sulfate and calcium sulfate in powder and dry form during the process. Because by adding iron sulfate in the presence of water, iron sulfate quickly turns into hydroxide and loses its reducing role in converting hexavalent chromium to trivalent chromium, and in this case, we will not have the ions needed to carry out the reaction.

In this method, iron sulfate was used as a reducing agent of hexavalent chromium to trivalent chromium, and finally, by adding calcium sulfate as the final precipitant, the complex required to remove hexavalent chromium was formed stably in the system. became. The retention time, the number of additives and the presence or absence of a stirrer can be mentioned as effective parameters on neutralization. Also, one of the important issues was neutralization of hexavalent chromium release from dust.

4. Conclusion

From the results of the tests and comparisons, it is understood that the co-precipitation method is an innovation in the deposition process and using the mentioned additives (iron sulfate, as a reducing agent of hexavalent chromium to trivalent chromium and calcium sulfate, to the title of the final precipitator) not only has an effective function in removing hexavalent chromium, but it can also reduce the content of trivalent chromium in solution to a significant amount, and this process is done with ease and relatively high speed. Another point is that the low dose of materials used, in addition to being cheap, has a high efficiency in removing and reducing high amounts of hexavalent chromium, which is a significant advantage compared to other materials and means further reduction of costs and reduction of waste materials. It is also important to create stable compounds that the presence of sulfuric acid in the long term cannot cause the re-release of hexavalent chromium and the return of the neutralization operation, and no hexavalent chromium is released by re-dissolving the neutralized dust in water.



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