Economic Method of Immobilization of Hexavalent Chromium in Contaminated Waste Treatment Using Waste Materials as Reagent

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Abstract:

Environmental pollution is a very important problem facing human influence worldwide. Waste management is a challenging task for the development of heavy metal processing technology, which is expensive. In rapid studies, hexavalent chromium has been reported in hazardous wastes treated with reagents such as ferrous sulfate, sodium thiosulfate, and sodium metabisulfite. Economically, these reagents are expensive for the metal to be converted from the hexavalent chromium form to the trivalent chromium form. We plan to reduce costs economically by using these waste materials like red clay and spent acid instead of reagents for conversion purposes in stabilization technologies. First check the concentration of hexavalent chromium using these waste material pathways and then verify that the hexavalent chromium is safely disposed of to the environment under stable and hazardous waste regulations using USEPA methods and HAZWAM guideline standard limits. Here, iron inclusions in red mud play a key role in converting Cr^{6+} to Cr^{3+} in acidic environments, eventually slightly increasing the pH of lime and combining with cement to protect the leachability of metals from soil and water contamination. The final conclusion is that the reduction of the leachability of hexavalent chromium in contaminated wastes is economically feasible at a very low cost and well established in an ecological concept.

Key words: Contaminated chrome waste, Innovative stabilization technologies, Red mud, spent acid, Lime and Cement.

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1. Introduction: -

Chromium is a naturally occurring element present in the textile industry during wastewater treatment as sludge. However, its most stable forms are trivalent (Cr^{3+}) and hexavalent (Cr^{6+}). The greatest variation in the physical, chemical and toxicological properties of chromium. But chromium (VI) is mostly produced from anthropogenic activities and highly toxic nature to living organisms. Cr^{6+} is easily soluble in water and can be contaminated in the environment. Chromium is used in many industrial applications in chrome plating, dye production, leather industry, textile industry, wood preservation. Most of the relevant chromium compounds such as chromate, dichromate, chromic acid, chromic sulfate, and chromic oxide. However, these industrial activities generate solid and liquid and chromium waste in atmospheric emissions. If Cr^{6+} increased concentration contaminated in water and soil can affect environmental pollution.

In many parts of the world, industries dispose of hazardous waste such as illegal dumps to the detriment of the environment and human health, and these waste dumps are a source of Cr^{6+} pollution and long-term groundwater damage. According to the World Health Organization (WHO), Cr(VI) is a highly carcinogenic group. The maximum permitted concentration of chromium in drinking water is 50 µg/l according to the guidelines. The USEPA recognizes that Cr (VI) is removed from wastewater by adsorption, chemical precipitation, ion exchange, electrocoagulation, membrane separation, and electro dialysis. But hazardous waste (contaminated waste) treated with sodium thiosulfate, ferrous sulfate, sodium met sulfate, etc. Hexavalent chromium is a well-known environmental contaminant that has the potential to cause cancer, teratogenicity, and mutations. The aim of the review is to reveal the harmful effects of Cr^{6+} and also to remediate the contaminated site by using waste material such as Red mud technology (instead of ferrous sulfate) to stabilize and decompose the pollutant $Cr^{6+.}$

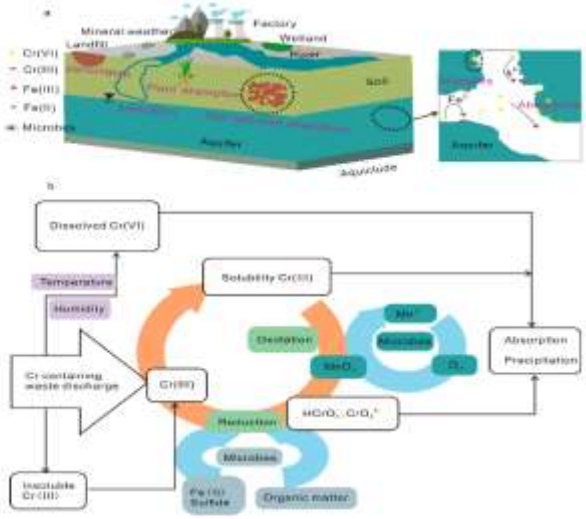


Figure 1. Shown the Flow diagram of effect on Eco System and Human Health due to high levels of Cr^{6+}

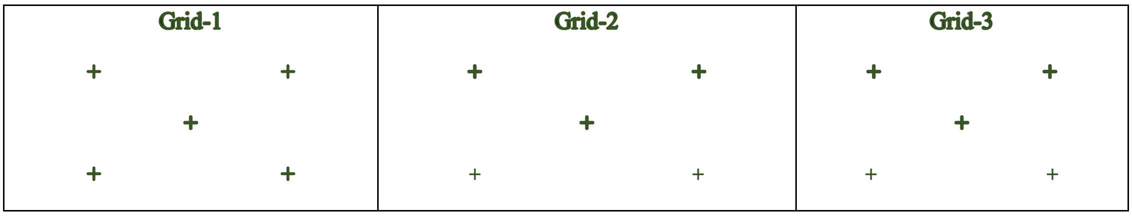
2. Materials & Methods:

2.1 Sampling collection:

We have collected samples randomly using equipment at different 11 locations and mixed each grid wise labelled all for homogeneously before start trials. We are divided complete area in Grid Wise Numbers-1 to 11, first we marked complete area as per Grids.

Each grid marking 4 corners and central take depth in 1 meter of each positions (total 5) then mixed as name A-1. Similarly dig 1 meter remaining each grid wise and mixed namely labelled from A2 to A11.

Figure 2. Shown the Grid Wise sampling map



Grid-11 + + + + +		**Grid-4** + + + + +
Grid-10 + + + + +	**Grid-8** + + + + +	**Grid-5** + + + + +
Grid-9 + + + + +	**Grid-7** + + + + +	**Grid-6** + + + + +

After collection of samples grinded without any lumps each samples in laboratory for homogeneously prepared before start the analysis and trails.

Figure 3. Shown the Sampling Photographs and Observation

2.2. WHO Standard Guideline's: -

The 1958 WHO International Standards for Drinking-Water recommended a maximum acceptable concentration of 0.05 mg/L for chromium (hexavalent) based on health concerns. This value was retained in the 1963 International Standard. Chromium was not evaluated in the 1971 International Standards. In the first edition of the Guidelines for Drinking Water Quality, published in 1984, a guideline value of 0.05 mg/L was retained for total chromium; Total chromium was specified because there were difficulties in analyzing only for the hexavalent form. The 1993 guideline questioned the guideline value of 0.05 mg/L because of the carcinogenicity of hexavalent chromium by the inhalation route and its Geno toxicity, although available toxicological data do not support the derivation of the new value. This guideline value was brought forward in the third edition of the guidelines published in 2004 and the fourth edition of the guidelines published in 2011. In a background document for the guideline published in 2020, additional chronic drinking water and mode-of-action studies were reviewed and the current guideline value of 0.05 mg/L was considered adequately health-protective for both cancer and non-cancer effects associated with hexavalent chromium. had come A second appendix to the fourth edition of the guidelines, incorporating this assessment, is expected to be published later in 2021.

Table 1. Criteria for Direct Disposal of Hazardous Waste into Secured Landfill

Leachate Quality	Concentration
pH	4-12
Total Phenols	<100 mg./l.
Arsenic	<1 mg./l.
Lead	<2 mg./l.
Cadmium	<0.2 mg /l.
Chromium-VI	<0.5 mg./l.
Copper	<10 mg./l.
Nickel	<3 mg./l.
Mercury	<0.1 mg./l.
Zinc	<10 mg./l.
Fluoride	<50 mg./l.
Ammonia	<1,000 mg./l.
Cyanide	<2 mg./l
Nitrate	<30 mg./l
Absorbable organic bound Chlorine	<3 mg./l
Water soluble compounds except salts	<10 %
Strength	
Transversal Strength (Vane Testing)	>25 KN/m^2
Unconfined Compression Test	>50 KN/m^2
Axial Deformation	<20 %
Degree of Mineralization or Content of Organic Materials (original sample)	
Annealing loss of the dry residue at 550^o C	<20 Wt. % (for non- biodegradablewaste) <5 Wt. % (for biodegradablewaste)
Extractable Lipophilic contents (Oil & Grease)	<4 Wt. %

Note: leachate quality is based on water leachate test i.e. Leachability tests are conducted by preparing a suspension of waste and water i.e. taking 100 gm of waste and filling up to 1 liter with distilled water, stirring or shaking for 24 hrs., filtering the solids and analyzing the filtrate.

2.3. Reagents Used: -

2.3.1. Ferrous Sulphate ($FeSO_4.7H_2O$):

Iron (II) Sulphate denotes arrange of salts data the formula $FeSO_4.H_2O$. The hydrated form is used medically to treat iron deficiency and also used industrial applications. It is a reducing agent such as used for the reduction of Chromium to less toxic Cr(iii) state. Ferrous Sulphate was used in the manufacture of inks, wood, dying, photographic developer.

Table 2. Shown the Analysis Report of Ferrous Sulphate

Physical properties	Unit	Result
Appearance	-	Faint blue to green
Form	-	Powder
Solubility	%	Clear
Assay	%	>99%
Molecular weight	g/mol	278
Density at 27°C	g/cc	1.89

2.3.2. Red Mud:

Red mud is generated during the processing of bauxite into alumina using the Bayer process. Main composition is various oxide compounds including the iron oxides which give its led condor. It's the high alkalinity nature. Its environmentally hazard due to its alkalinity (high pH >12).

Table 3. Shown the Analysis report of Red mud

S.No.	Test Parameter	Result (%)
1	Loss on Ignition	12.6
2	SiO_2	14.1
3	Al_2O_3	20.7
4	Fe_2O_3	44.2
5	CaO	1.1
6	MgO	0.27
7	Na_2O	5.8
8	K_2O	0.29

2.3.3. Spent Acid:

It is the received from industries i.e., spent acid. Specific gravity is 1.22 (approx.)

2.3.4. LIME

It is usually by the thermal decomposition of materials such as Lime stone that contains Calcium carbonate in lime kiln. By heating the material above 825^{0}C a process is called Calcination or lime burning, to liberate a molecule of carbon dioxide. It is useful for waste water treatment and stabilization of hazardous waste. Limestone also used for cement industries. Lime cost approx. 5500 per MT. and easily available in market.

$$\underset{\text{Calcium carbonate}}{CaCo_3\,(s)} \;\text{-----------}\; \underset{\text{Calcium Oxide}}{CaO\,(s)} + \underset{\text{Carbon dioxide}}{CO_2\,(g)}$$

Table 4. Shown the Analysis report of Lime

S.No.	Parameter	Unit	Result
1	Appearance	Visual	White
2	Available as CaO	%	65.1

3	Available as $Ca(OH)_2$	%	85.9
4	Acid insoluble	%	0.26
5	Moisture as free water	%	0.42
6	Magnesium as MgO	%	1.32

2.3.5. CEMENT:

Cement is fine powder when mixed with water, set to a hard mass. Setting and hardening result from hydration, which is a chemical combination of the cement compounds with water that yields submicroscopic crystals or a gel-like material with a high surface area. Because of their hydrating properties, constructional cements, which will even set and harden under water, are often called hydraulic cements. The most important of these is Portland cement. Cement cost approx. 6000 per MT and available market from dealers based on the quality.

Table 5. Analysis report of Cement

S.No.	Parameter	Unit	Result
1	Appearance	Visual	Grey
2	Loss on Ignition	%	1.27
3	CaO	%	85.9
4	SiO_2	%	0.26
5	Al_2O_3	%	0.42
6	MgO	%	1.32
7	Fe_2O_3	%	0.12
8	P_2O_5	%	0.09
9	K_2O	%	0.07
10	Mn_2O_3	%	0.01
11	ZnO	%	0.002
12	TiO_2	%	0.08

2.4. Sample preparation:

Take WLT sample 0.5ml acidify with acid maintain pH <2 make up to with distilled water add 2ml Diphenyl carbazide solution. After develop colour wait 10 minutes' measure at 540nm Cr^{6+} concentration by UV – VIS spectrometer.

2.5. Preparation of Water Leachate Test:

Take above stabilized trail samples 10% add with distilled water (10g sample in 100 ml water). Keep it in plat form shaker for mixing 24 hours continuously. After mixing of all samples remove from shaker filter it in conical flasks. After that filter the leachate test to Cr^{6+} on UV-VIS spectrophotometer by calorimetry (APHA method).

Figure 4. Preparation of Samples for Leachate Test

3. Results and Discussion: -

3.1. Analysis of Contaminate Waste:

Initially analyze the waste as per the USEPA methods both physical and chemical properties. Results are given below the Table 6.

Table 6. Physical and Chemical analysis of Contaminated waste

S. No.	Sample description	pH	Loss On Drying (%)	Cr^{6+} in WLT (ppm)
1	Contaminated waste (A1)	12.37	15.93	168
2	Contaminated waste (A2)	12.57	18.76	141
3	Contaminated waste (A3)	12.48	12.98	156
4	Contaminated waste (A4)	12.3	11.17	242
5	Contaminated waste (A5)	12.35	15.91	297
6	Contaminated waste (A6)	12.47	17.01	187
7	Contaminated waste (A7)	12.97	16.12	301
8	Contaminated waste (A8)	12.95	21.54	124
9	Contaminated waste (A9)	12.97	21.53	152
10	Contaminated waste (A10)	12.88	22.52	126
11	Contaminated waste (A11)	12.67	22.92	159
Average				187
Maximum				301
Minimum				124
Landfill Limit (WLT)				**<0.5**

Figure 5. Hexavalent chromium testing by UV-VIS spectrometer

3.2. Design of experiments:

Based on the above Cr+6 result not fit for direct landfill as per CPCB protocol(guidelines). WLT limit of Cr^{6+} is <0.5 ppm. It is observed range between **124 to 301 ppm** accordingly. Trails are conducted initially with ferrous Sulphate and Sulphuric acid for conversion of chromium Cr^{6+} to Cr^{3+} then neutralize with lime pH up to 8 finally binding with cement. Conduct the WLT test after stabilized samples for Cr^{6+}. It is observed Cr^{6+} <0.5ppm.

Note: In Waste contains Hexavalent chromium is observed is very high level. We are trails with Ferrous Sulphate and optimized and final recipe as per below: -

"30% Sulphuric acid, 30% Ferrous Sulphate, 30% Lime & 50% Cement"

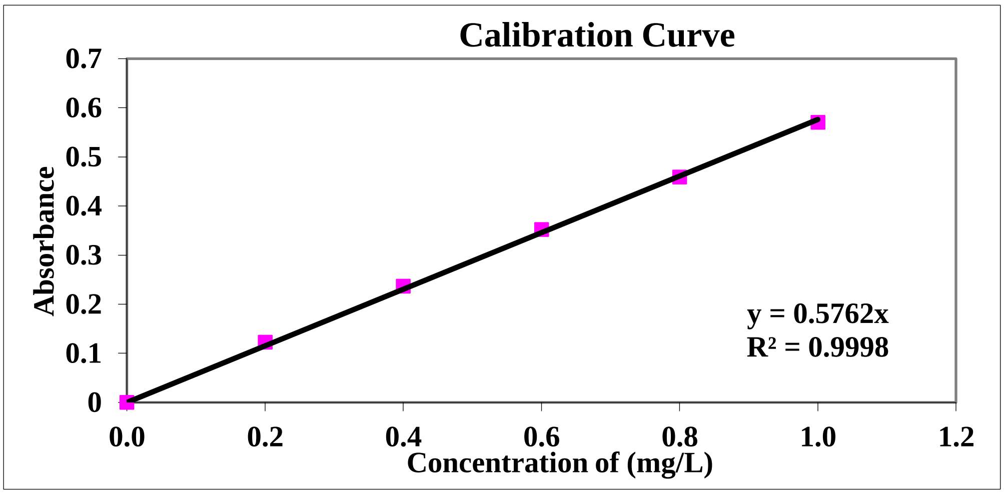
3.3. Standard preparation (1000ppm):

Prepare working standards from stock standard of Chromium (1000ppm). Initially make diluted to 100 ppm (10 to 100ml). Again dilute to 10 time it's become 10 ppm. From this take 2.0, 4.0, 6.0, 8.0 & 10.0 ml diluted to 100 ml flasks. Now our Chromium standards are 0.2, 0.4, 0.6, 0.8 and 1.0 ppm respectively. Using these standards make the graph before that using reagent blank also prepare for remove if any error or interference in reagents. Calibrated the graph check the correlation coefficient should be more than 0.995. If calibration graph is ok now aspirate the trail samples WLT sample concentration in stabilized samples.

Table 7. Standard Preparation

Sl. No.	Standard solution (mg/L)	Dilution (ml)	Standard (mg/L)	Reading
1	2	100	0.2	0.1226
2	4	100	0.4	0.2365
3	6	100	0.6	0.3521
5	8	100	0.8	0.4586
6	10	100	1.0	0.5704

Figure 6. Graph shown the Calibration curve



Results are observed within acceptance criteria of Cr6+ is below 0.5 ppm as per Land fill criteria (CPCB guidelines).

Table 8. Design with Red mud and Spent acid

S. No.	Trial No.	Waste (g)	Spent acid (%)	Red Mud (%)	Cement (%)	Lime (%)	Cr^{6+} in Water Leachate Test (ppm)	Status
1	01	20	40	20	50	30	2.89	Fail
2	02	20	40	40	50	30	2.56	fail
3	03	20	50	40	50	30	1.19	Fail
4	04	20	50	50	50	30	0.98	Fail
5	05	20	60	50	50	30	1.03	Fail
6	06	20	60	60	50	30	0.88	Fail
7	07	20	70	40	40	30	0.75	Fail
8	08	20	70	50	50	30	0.48	Pass
9	09	20	70	50	60	30	0.40	Pass

Figure 7. Confirmation trials

3.4. Final Recipe:

Optimization of trails with 70% spent acid, 50% red mud, 30% lime and 50% cement. After stabilized trials conducted WLT for Cr^{6+} on UV-VIS spectrometer observed within CPCB landfill limit (i.e. Cr^{6+}<0.5ppm).

Table 9. Optimization of Trails

S. No.	Waste (g)	Spent acid (%)	Red Mud (%)	Lime (%)	Cement (%)	Cr^{6+} in WLT (ppm)	Cr^{6+} limit (CPCB) ppm
1	20	70	50	30	50	0.48	<0.5
2	20	70	50	30	50	0.42	
3	20	70	50	30	50	0.44	

3.5. Cost calculations:

Table 10. Rates of Reagents

Reagent	**H_2SO_4**	**$FeSO_4$**	**Spent acid**	**Lime**	**Cement**	**Red Mud**
Cost per MT	**10000**	**6500**	**0**	**5500**	**6000**	**0**

Table 11. Treatment composition for 1 MT waste

Reagents	Treatment with $FeSO_4$ (%)	Treatment with Red mud (%)
Sulphuric acid	30	0
Spent acid	0	70
$FeSO_4$	30	0
Red mud	0	50
Lime	30	30
Cement	50	50

Table 12. Treatment cost of MT Waste with FeSO4 and Red Mud in Indian Rupees

Reagents	Cost with $FeSO_4$ per MT (Rs.)	Cost with Red Mud per MT (Rs.)
Sulphuric acid	3000	0
Spent acid	0	0
$FeSO_4$	1950	0
Red Mud	0	0
Lime	1650	1650
Cement	3000	3000
	9600	**4650**

4. Recommendation and Conclusion:

- Treatment cost variation between reagents both $FeSO_4$ and Red Mud is Rs/- 4950 per MT Cr^{6+} in this stabilization trails.
- Resources of ferrous Sulphate consumption to be avoid environmental friendly manner.

- Overall saving of cost per MT approximately Rs/- 5000 for treatment of hexavalent chromium in higher level concentration.
- The above optimization of recipe is meet the acceptance criteria of landfill as per CPCB guidelines.
- We have observed iron content in Red Mud its very useful conversion of Cr^{6+} state to Cr^{3+} (stable state). It is act as a good reductant role for treatment.

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- Health hazards of hexavalent chromium (Cr (VI)) and its microbial reduction Pooja Sharmaa,b,1 , Surendra Pratap Singhc,1 , Sheetal Kishor Parakha,b, and Yen Wah Tonga,b,d a Environmental Research Institute, National University of Singapore, Singapore; b Energy and Environmental Sustainability for Megacities (E2S2) Phase II, Campus for Research Excellence and Technological Enterprise (Create), Singapore; c Plant Molecular Biology Laboratory, Department of Botany, Dayanand Anglo-Vedic (PG) College, Chhatrapati Shahu Ji Maharaj University, Kanpur India; d Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore
- Hexavalent Chromium Removal from Water and Wastewaters by Electrochemical Processes: ReviewI¸sık Kabda¸slı *and Olcay Tünay Environmental Engineering Department, Civil Engineering Faculty, Istanbul Technical University, Ayaza ˘ga Campus, Istanbul 34469, Turkey Correspondence: kabdasli@itu.edu.tr; Tel.: +90-212-285-65-86