

# Experimental Validation on the Treatment of Contaminated Ground Water at COPR Dump Site

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## Abstract

The suitability of sulphate and sulphite salts for the remediation of contaminated ground water at laboratory scale is reported in this paper. Studies reveal that the amount of sulphate salt consumed is greater than the amount of sulphite salts. The efficiency of sulphite salt is more at pH-2 whereas for sulphate salt it is at pH-2.5. An anomaly in the behaviour of sulphite salt in the reaction environment is noticed. However, complete reduction of Cr(VI) to zero level is reported without dilution in the contaminated ground water. Data obtained are compared with previous work with  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{SnCl}_2$ . Best reducing agent for complete removal of hazardous Cr(VI) at COPR dump site is proposed. Site remediation highlighted could solve the problems of COPR dump sites exist worldwide and could produce water for industrial purpose.

**Keywords:** Contaminated groundwater; Hexavalent Chromium; Sodium sulphite; Sodium bi sulphite; sodium meta bisulphite; Ferrous sulphate; Reduction of Cr(VI) and COPR.

## INTRODUCTION

The atomic density of heavy metals is greater than water by  $4000 \text{ kgm}^{-3}$ . The heavy metals exist in most stable oxidation states may get solubilised in ground water through natural processes or by change in soil pH due to anthropogenic activity [1]. Level of such metals at minimum concentration act as essential micro nutrients for human beings and at higher concentrations they become poison [2]. Enzymes and biological fluid on reaction with such heavy metals give irreversible material that destroys the metabolic activities [3-4].

Unlike organic contaminants such as pesticides or petroleum by products, heavy metals pollute the environment and are more persistent [5]. Chromium is one such metal having different oxidation state, from Cr (I) to Cr (VI). Among them the more stable form are Cr(VI) and Cr(III). Increased temperature, pressure, moisture and pH maintained inside the earth surface cause the mobility and reactivity [6]. As a result, a fraction of the total mass of Cr(VI) leach into aquifer[7]. Thus the hazardous Cr(VI) contaminated water becomes available to living organisms via food chains[8].

In the past two decades, the COPR site at Ranipet, Vellore, Tamilnadu, India concerned the devastating effect of groundwater contamination and threat to the living community of the area [9]. Intrusion of underground-water flow causes the transport of metal contaminants. Leachate from the COPR dump site penetrate through the land and accumulated in the aquifers, which raises the concentration of Cr(VI) in ground water[10].

Various literatures were published on the technologies that were applied all over the world to remediate the contaminated soil and aquifers[11].The treatments include degradation, extraction, stabilization, separation and containment of the polluted material from exposure to wider environment[12]. Yang and sun,[13] have shortlisted several soluble reducing agents such as sulphite, thiosulphate, hydroxylamine, dithionite, hydrogen sulphide, Fe(0) and Fe(II) for reduction of Cr(VI) to Cr(III). There are possibilities for conversion of Cr (III) to Cr (VI) by the influence of environment. It is therefore essential to remove both Cr(III) and Cr (VI) from the treated water to protect the environment .

The decision on site specific groundwater remediation is a challenging task, due to the uncertainty in assessment of level of contamination, soil permeability, groundwater flow pattern, complex chemical processes taking place in the aquifer impacts of the technique on the environment and cost of treatment process [14]. Malaviya and Singh,[15] narrated that soil composition, geological feature, interactions between remediation technologies and the concentration of active contaminants should be considered before implementing remediation plans on groundwater contaminated areas.

A study conducted by the Geological Survey of India in 1996 reported that Cr(VI) contamination spreads in south up to Karai village, which is located 1.5 km from the factory which might have extended now beyond that also[16]. Report submitted by National Environmental Engineering Research Institute and National Geophysical Research Institute confirms the effect of TCCL site on the environment [17]. In 2011, Ligy Philip et al,[18] proposed a mathematical models for clean-up of Cr(VI) contaminated aquifers using bioremediation.

In this paper, the suitability of sodium sulphite, Sodium bi sulphite, Sodium meta-bisulphite and ferrous sulphate at various pH are reported. A pilot scale study planned to be carried out at TNCCL site is proposed.

## MATERIALS AND METHODS

### Materials

All analytical grade chemicals used in this study were purchased from E-Merk India Ltd and used as such. Potassium dichromate ( $K_2Cr_2O_7$ ) was used for the preparation of synthetic Cr(VI) water. Sulphite, bi sulphite, and meta-bisulphite salts of sodium as well as sulphate of iron were adopted as reducing agents. The reduction pH was adjusted using 1N  $H_2SO_4$  and precipitation pH was adjusted using 1N sodium hydroxide (NaOH). High purity distilled water was used to make up all solutions. The pH was determined using pH meter 240 (Elico L1614). The concentration of Cr(VI) was determined by recording the absorbance at 540 nm using UV-Visible Spectro photometer (UV - 3200, Lab India).

### Chromium Contaminated Groundwater

The samples of chromium contaminated groundwater (CGW) were collected in the month of May 2016, from a monitoring well of 7 cm diameter and 25 m depth in the COPR dump site. The seasonal variation influences the concentration of chromium in the groundwater. The samples were collected in polypropylene containers. The Cr(VI) concentration varied with depth and was in the range of 1,111  $mgL^{-1}$  to 2000  $mgL^{-1}$ . The filtered samples were used for analysis. The parameters such as turbidity, total dissolved solid and electrical conductivity were analysed for the sample containing 2000  $mgL^{-1}$  of Cr(VI) and were found to be 195 NTU, 5000  $mgL^{-1}$  and 7580  $\mu s/cm$  respectively. The other parameters observed are presented in Table-1.

**Table 1.** Characteristics of groundwater

S. No.	Description	Value
(a)	pH	6.5
(b)	BOD 5 days 20°C in $mgL^{-1}$	15
(c)	COD in $mgL^{-1}$	100
(d)	Total suspended solids in $mgL^{-1}$	20
(e)	Total dissolved solids in $mg L^{-1}$	5000
(f)	Total Chromium in $mgL^{-1}$	2166
(g)	Hexavalent Chromium in $mgL^{-1}$	2000
(h)	Colour	Brownish Yellow

### Synthetic Contaminated water

Since the CGW contains a maximum of 2000  $mgL^{-1}$  of Cr(VI), the concentration of Cr(VI) in the SCW is brought to 2000  $mgL^{-1}$  by dissolving 5.658 g of  $K_2Cr_2O_7$  in 1000ml distilled water.

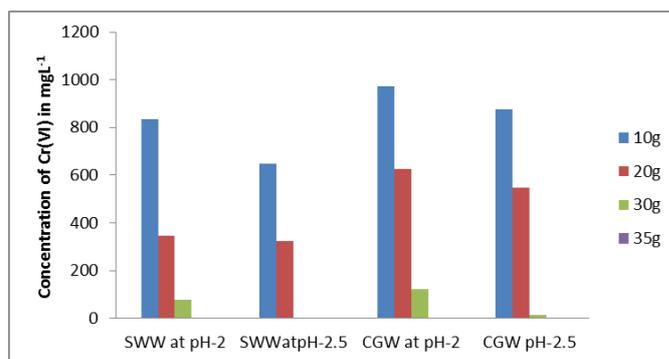
## RESULTS AND DISCUSSION

Sulphur dioxide was used in small and medium-sized Effluent Treatment Plants as reducing agents [17]. Being gaseous and toxic in nature much care should be taken in working area to prevent health problem to workers from inhalation of the

sulphur dioxide. Installation of vacuum system is necessary to overcome the health problem of workers. Hence,  $SO_2$  is not tried in this study.

### Effect of Ferrous sulphate at various pH.

The amount of  $FeSO_4$  consumed for complete reduction of Cr(VI) in SCW and in CGW containing 2000  $mgL^{-1}$  of Cr(VI) was 35  $gL^{-1}$ . The data obtained for the addition of 10 g, 20g, 30 g, 35 g and 40 g are presented in Fig-1.

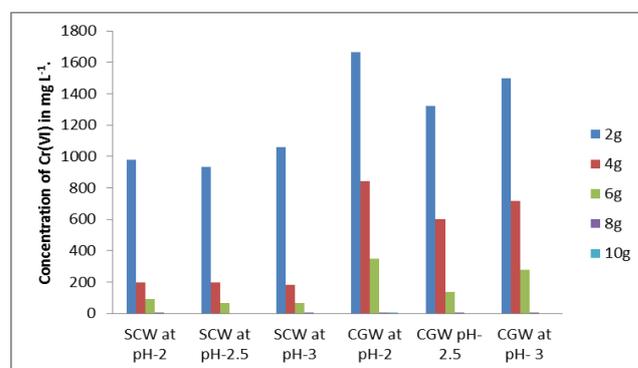


**Figure 1.** Reduction of Cr(VI) in SCW and CGE at various pH using  $FeSO_4$

The amount of  $FeSO_4$  required for complete reduction in this study is very high when compared to our earlier report using  $Na_2S_2O_5$  and  $SnCl_2$ [19]. So attempts were made with other sulphite chemicals.

### Effect of Sodium Meta bisulphite at various pH.

The reduced value of Cr(VI) noticed for CGW after the addition of the various amount of  $Na_2S_2O_5$  ( 2 g, 4g, 6g, 8g, 10 g and 12 g) at pH-2 were 1664.7  $mg L^{-1}$ , 842  $mg L^{-1}$ , 347  $mgL^{-1}$ , 36  $mgL^{-1}$ , 2.78  $mgL^{-1}$  and 0.0132  $mgL^{-1}$ . At pH-2.5 the amount noticed for the above said amount of  $Na_2S_2O_5$  were 1321  $mgL^{-1}$ , 603  $mgL^{-1}$ , 138  $mgL^{-1}$ , 1.190  $mgL^{-1}$  and 0.0  $mgL^{-1}$ . At pH-3 the observed values were 1499  $mgL^{-1}$ , 715  $mgL^{-1}$ , 280  $mgL^{-1}$ , 4.85  $mgL^{-1}$ , 0.35  $mgL^{-1}$  and 0.0  $mgL^{-1}$ . The above data presented in Fig-2 exposes that the reduction efficiency of  $Na_2S_2O_5$  is maximum at pH-2.5.

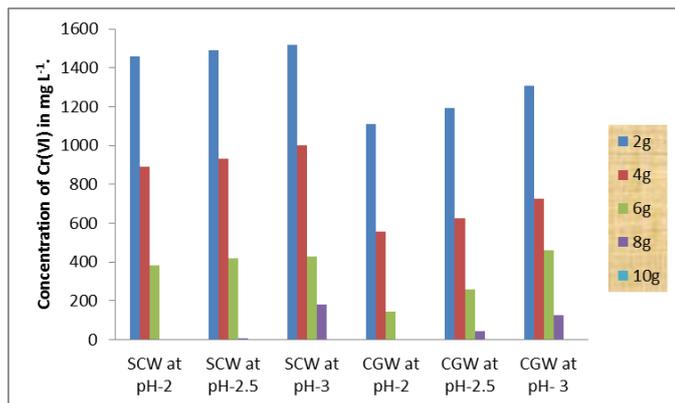


**Figure 2.** Reduction of Cr(VI) in SCW and CGE at various pH using  $Na_2S_2O_5$

For  $\text{FeSO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_5$  the complete reduction of Cr(VI) is noticed at pH-2.5 and the amount required at this conditions are 35g and 10g respectively.

**Effect of Sodium bi sulphite at various pH.**

At pH-2, 2.5 and 3, the amount of  $\text{NaHSO}_3$  added in SCW were 2.0  $\text{gL}^{-1}$ , 4.0  $\text{gL}^{-1}$ , 6.0  $\text{gL}^{-1}$ , 8.0  $\text{gL}^{-1}$  and 10.0  $\text{gL}^{-1}$ . Similar attempts were executed to contaminated ground water containing 2000  $\text{mgL}^{-1}$  of Cr(VI) and the results are presented in Fig.3.

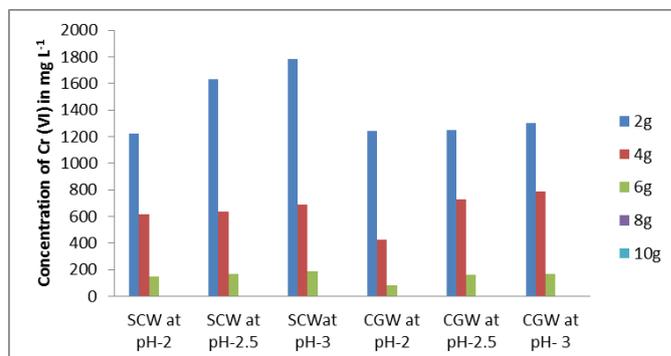


**Figure 3.** Reduction of Cr(VI) in SCW and CGW at various pH using  $\text{NaHSO}_3$ .

From the fig-3 it is observed that complete removal of Cr(VI) occurred at pH-2 for 8.0 g addition of  $\text{NaHSO}_3$ . At the same dosage the concentrations of Cr(VI) was found to be 5.1  $\text{mg L}^{-1}$  at pH-2.5 and 180  $\text{mg L}^{-1}$  at pH-3. Contrary to the previous observation made by us [18] and in the present study (using  $\text{FeSO}_4$ , and  $\text{Na}_2\text{S}_2\text{O}_5$ ) the efficacy of  $\text{NaHSO}_3$  seems to be higher in CGW.

**Effect of Sodium sulphite at various pH.**

Conditions adopted for  $\text{NaHSO}_3$  were utilised for  $\text{Na}_2\text{SO}_3$ . To find out the reason for more efficiency of reducing agent in CGW, the chloride and sulphate ions concentrations were increased by adding  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  in SCW and the results observed are presented in Fig.4.



**Figure 4.** Reduction of Cr(VI) in SCW with added ions and CGW at various pH using  $\text{Na}_2\text{SO}_3$ .

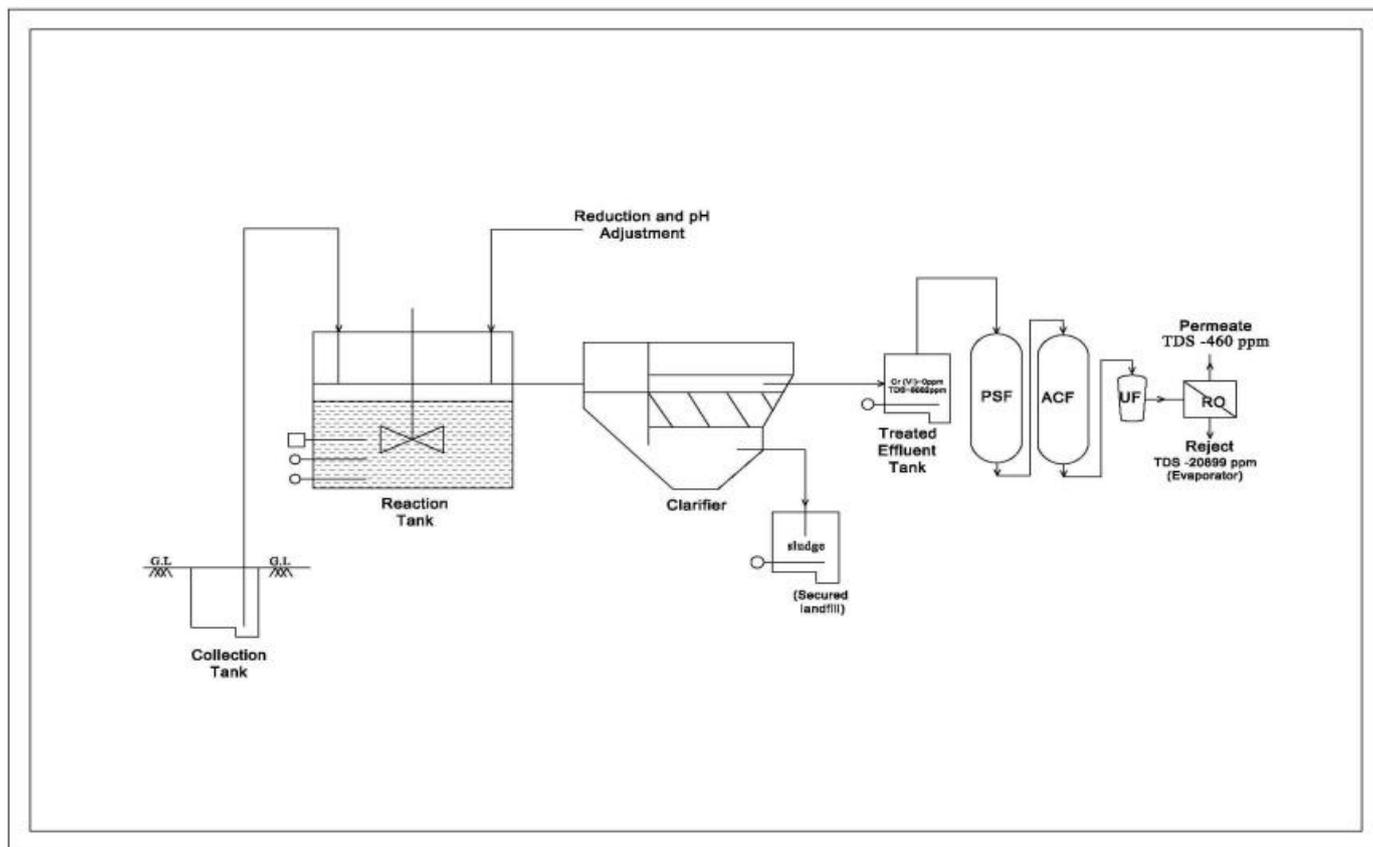
Each test was in triplicate and the average was shown as the final result. The amount of Cr(VI) recorded after adding 2  $\text{gL}^{-1}$ , 4  $\text{gL}^{-1}$ , 6  $\text{gL}^{-1}$  and 8  $\text{gL}^{-1}$  of  $\text{Na}_2\text{SO}_3$  to the SCW sample containing 2000  $\text{mgL}^{-1}$  of Cr(VI) were 1225  $\text{mgL}^{-1}$ , 615  $\text{mgL}^{-1}$ , 152  $\text{mgL}^{-1}$  and zero at pH-2. Under the same conditions the amount observed were 1635  $\text{mgL}^{-1}$ , 635  $\text{mgL}^{-1}$ , 170  $\text{mgL}^{-1}$  and zero for pH-2.5 and 1786  $\text{mgL}^{-1}$ , 687  $\text{mgL}^{-1}$ , 186  $\text{mgL}^{-1}$ , 0.32  $\text{mgL}^{-1}$  and zero for pH-3.

The study was extended to the CGW containing 2000  $\text{mgL}^{-1}$  of Cr(VI) and the data obtained are presented in Fig.4. Reasons for more efficacies of  $\text{NaHSO}_3$  and  $\text{Na}_2\text{SO}_3$  in CGW could not be solved in this attempt. Further studies on these lines are under progress. To find out the best reducing agent among all the reducing agents used in our studies [20-21] the data obtained are presented in Table-2.

**Table 2.** Comparative study of various chemicals used in TCCL site.

SL. NO	Reducing agent	Dosage of reducing agent (g)	Reduction pH	Volume of 1N $\text{H}_2\text{SO}_4$ Consumed (ml)	Precipitation pH	Volume of 1N $\text{NaOH}$ consumed (mL)	Conc. of Cr(VI) in the filtrate	Weight of sludge (g)
1	$\text{Na}_2\text{S}_2\text{O}_4^*$	4.5	2.5	48	9	87	0	11.5
2	$\text{Na}_2\text{SO}_3$	8	2	62	9	104	0	13.8
3	$\text{NaHSO}_3$	8	2	154	9	122	0	11.08
4	$\text{Na}_2\text{S}_2\text{O}_5$	10	2.5	58	9	106	0	15.5
5	$\text{SnCl}_2^*$	14	Nil	0	9	135	0	26.38
6	$\text{FeSO}_4$	35	2.5	163	9	440	0	39

\*values are taken from our previous report [20-21]



**Figure 5.** Effluent Plant Treatment System

Based on the above chemicals it is observed that sodium di thionite is the bet suitable chemical for the reduction at this site. A pilot scale study was carried out using 100 lit of CGW in a treatment system comprising collection tank, reaction cum settling tank, Clarifier, treated effluent collection tank, pressure sand filter, activated carbon filter, ultra filtration , R.O plant and evaporator. Reject from Stage I, II and III are allowed to pass through the two stage micron filter for removal of fine suspended particles up to 5 micron level.

Based on the results obtained in the pilot scale study, a design calculation was carried out to treat 25,000 L/d of CGW. The total area required for various tanks are provided in Table III.

**Table III:** Area Requirement

Sl. No.	Description		Area in m <sup>2</sup>
1	Collection Tank	4.0 x 4.0 x 2.5 m	20
2	Flocculation Tank	2.0 m Dia x 1.5m	4
3	Mixing Channel	20.0 x 1.0 x 0.15 m	10
4	Primary Settling Tank & Lamella Plate separator	20.0 x 1.0 x 0.15 m and 1.5 x 1.5 x 2.5 m	15
5	Intermediate Collection Sump	3.0 x 3.0 x 2.5 m	10
6	Pressure Sand Filter	0.5 m Dia x 2.0 m HOS	2
7	Activated Carbon Filter	0.5 m Dia x 2.0 m HOS	2

Sl. No.	Description		Area in m <sup>2</sup>
8	Treated Effluent Collection Sump (RO Feed Sump)		10
9	Sludge Drying Beds	80 Sq. m	80
10	RO Stage I, II and II Reject Tank s	3.0 x 3.0 x 2.5 m (each)	24
11	RO Product water Tank		10
12	<b>Solar Evaporation Pans</b>	140 Sq. m	140
13	RO Plant IV Stages		80
14	Mechanical Evaporator		20
	<b>Total</b>		<b>437</b>

### RO PLANT

**Stage I:** The system is designed to treat the CGW of 5.0 KL/hr with TDS around 8000 – 10,000 mg L<sup>-1</sup> for a recovery of 60% permeate.

**Stage II:** The system is designed to treat the reject obtained in stage-I. Flow rate of 2.0 KL/hr with TDS around 12000 – 14000 mgL<sup>-1</sup> for the recovery of 50% of permeate.

**Stage III:** The system is designed to treat the reject obtained in stage-II. Flow rate of 1.0 KL/hr with TDS around 22000 – 24000 mgL<sup>-1</sup> for a recovery of 40% of permeate.

**Mode of Disposal:** Total permeates water from the RO Plant would be 22.0 KLD which could be utilized to any other industry located within the area. RO reject feed flow 3.0 KLD would be fed into mechanical evaporator (Double Effect with boiler steam). Expected evaporation is 80% (2.4 KLD). Evaporator reject 20% (0.6 KLD) would be disposed to elevated solar evaporation pans for natural evaporation pan. The residue could be treated by solidification and stabilization process reported by us[22].

## CONCLUSION

The observation reported in this paper exposes that sulphite salts are more efficient than sulphate salt for the reduction of Cr(VI) to Cr(III). In sulphite salts the oxidation of sulphur might have caused the reduction of Cr(VI) and in sulphate salts the oxidation of metal ions causes the reduction of Cr(VI). The amount of sulphite salts required is lower than the amount of sulphate salt. Comparison of our earlier reports with present analysis reveals that  $\text{Na}_2\text{S}_2\text{O}_4$  is the best reducing agent for complete removal of hazardous Cr(VI). Site remediation proposed in this study could solve problems of COPR dump sites exist worldwide and could produce water for industrial purpose.

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