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Decontamination of Hexavalent Chromium by Geo Chemical Fixation Method in a Hazardous Dump Site, Ranipet, Tamil Nadu, India

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Abstract: Tanneries in an industrial area of Ranipet (India) manufactured sodium bi-chromate crystals and chromium sulphate tanning powder during 1976-1996. Tamil Nadu Chromate and Chemicals (TCCL) factory generated approximately 1,60,000 m ton of chromium waste which is dumped in the factory premises to a height of 2-4 m of Hexavalent chromium Cr (6). Disposal of this waste face a threat to the people residing in around the area for 40 years. Disposal of the chromium waste is the great problem to be addressed. It was observed that the Hexavalent chromium contamination reached to a depth of 15 m in the upstream of the dyke and in the downstream to a depth of 8-10 m. The migration of Hexavalent chromium is very slow with a ground water velocity of 10 m/year. The sludge is mixed with the soil and the ground water being contaminated with chromium. Because of this environmental effect we had taken initiative to make remediation onsite. As a remedial measure an onsite Geo chemical fixation method may be adopted for decontamination of hexavalent chromium.

Key words: Physio-chemical parameters, water contamination, hexavalent chromium, total chromium, hexavalent, contaminated

INTRODUCTION

Chromium is utilized in industrial activities like electroplating, fertilizers, varnish and metallurgy which is a major contaminant from the tanning industry. Chromium is water soluble and extremely toxic to the human body tissue. Breathing chromium (6) irritates the nose or mouth of the people which also cause asthma and lung cancer. With the increase in sense of awareness about the environment, researchers focus the study of transport related to ground water contamination (Mertz *et al*., 1974; Baes and Robert, 1976; Ringstad *et al*., 1990; Govil *et al*., 2004).

TCCL factory was started in 1976 and its main products are sodium bi-carbonate crystals and chromium sulphate tanning powder. Tamil Nadu Pollution Control Board (TNPCB) made a report in 1996 estimated that 1,60,000 tonnes of solid chromium waste to a depth of 2-4 m in an area of 8.6 acres of land within TCCL premises. The leachate generated from infiltration of rain water pollutes the ground water downstream areas. Soil and geological formation containing higher levels of chromium can leach those metals into the ground water. This can be moved by pumping wells particularly for agriculture. Health effects from contaminated ground water depends upon the specific pollutant.

Study area: The study area is located 3 km North West of Ranipet on NH 4 highway to Bangalore lies Northern latitude 12°55'0-12°58'0" and Eastern longitude of 79°17'30"-79°20'0" and falls in Survey of India Topo Sheet No. 57-P/5. This study area is 116 km from Chennai and 43 km before Chittor District of Andhra Pradesh and sited in Plot No. 25 of SIPCOT industrial estate along the NH4 Ranipet, Chennai. Topography of the watershed varies from 190-162 m Above Mean Sea Level (AMSL).

Geomorphologically, the area depicts undulating topography falling in pediment zone of the denudational and structural hills rising in the northern side. The flat to undulating pediplain nature continue and extends up to the flood plain of Palar River. Near the TCCL dump site the NH4 national highway acts as the boundary between the hard rock and alluvial environ. Preliminary geological studies were carried out by Geological Survey of India (GSI., 1997) and NGRI in 2005. The study area of 42.3 km^2 is mapped in Fig. 1 and 2.

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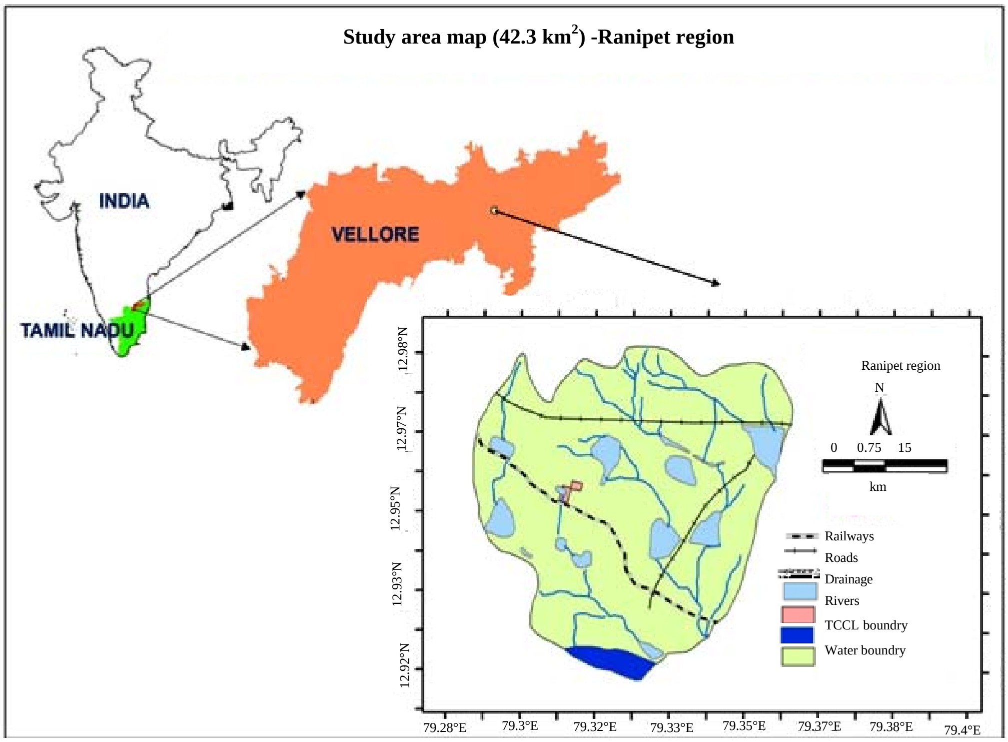

Fig. 1: Location map of Ranipet watershed area, Tamil Nadu

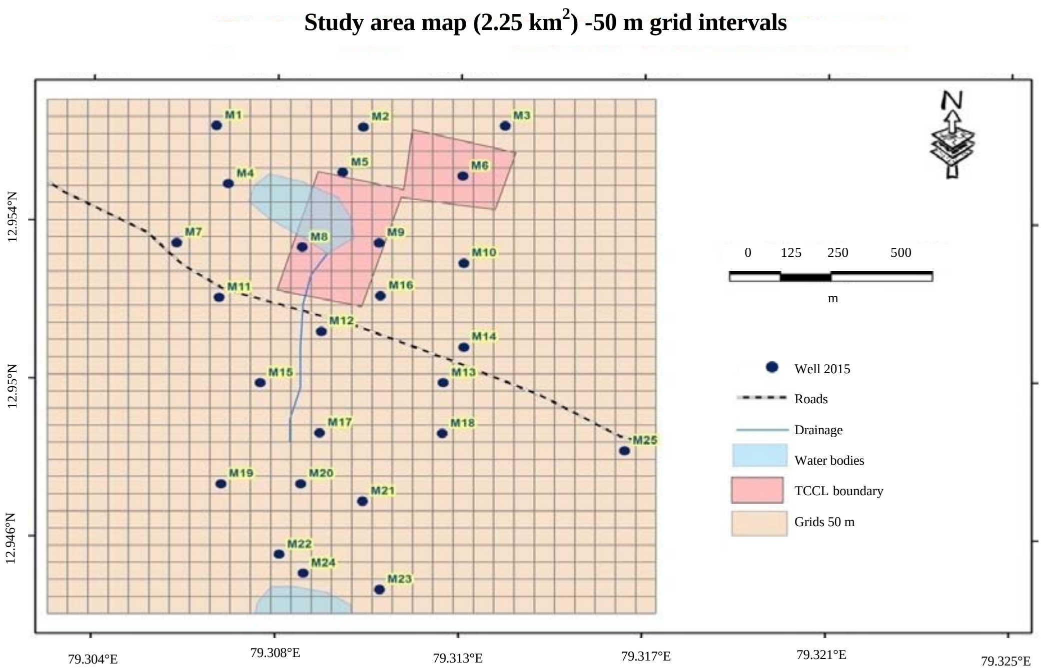

Fig. 2: Total area of contamination in the watershed

MATERIALS AND METHODS

A total of 25 bore holes were drilled in and around the dump site of different locations and the water samples were collected in 2 L plastic cans. The location of bore holes are shown in Fig. 2. A total of 8 bore holes were drilled into the premises of TCCL site where others in the open land around the TCCL site. The water samples

Table 1: Physico-chemical characteristics of water samples

Standard	p_H	Cr^{6+}(mg/L)	Total Cr (mg/L)
WHO	7-8	0.05	0.05
ISI 10500-91 standard	6.5-7.5	0.05	0.05

Table 2: pH, Cr^{6+} and total chromium concentrations in bore wells 2015

Well No.	Latitude	Longitude	pH	Cr^{+6} (mg/L)	Total chromium (mg/L)
M1	12°57'24.01"	79°18'25.2"	7.4	<0.01	0.07
M2	12°57'23.93"	79°18'37.21"	7.4	<0.01	0.06
M3	12°57'24.11"	79°18'48.8"	7.6	<0.01	0.06
M4	12°57'18.49"	79°18'26.19"	7.7	<0.01	0.07
M5	12°57'19.61"	79°18'35.54"	9.1	64.06	21.23
M6	12°57'19.31"	79°18'45.37"	7.2	<0.01	0.06
M7	12°57'12.86"	79°18'22.01"	6.8	<0.01	0.06
M8	12°57'12.5"	79°18'32.28"	11.0	142.30	28.47
M9	12°57'12.94"	79°18'38.56"	9.3	29.65	18.26
M10	12°57'11.06"	79°18'45.51"	7.1	<0.01	0.06
M11	12°57'7.69"	79°18'25.51"	7.1	<0.01	0.07
M12	12°57'4.51"	79°18'33.89"	8.0	1.06	1.05
M13	12°56'59.59"	79°18'43.9"	6.7	<0.01	0.06
M14	12°57'17.92"	79°18'45.56"	6.6	<0.01	0.05
M15	12°56'59.59"	79°18'28.94"	6.7	<0.01	0.05
M16	12°57'7.92"	79°18'38.72"	8.1	38.46	19.05
M17	12°56'54.87"	79°18'33.82"	10.2	92.50	21.08
M18	12°56'54.86"	79°18'43.86"	7.1	<0.01	0.05
M19	12°56'49.97"	79°18'25.78"	8.1	22.08	17.17
M20	12°56'50.01"	79°18'32.31"	7.5	18.06	16.05
M21	12°56'48.39"	79°18'37.38"	6.6	<0.01	0.05
M22	12°56'43.3"	79°18'30.59"	8.1	81.20	24.80
M23	12°56'40.02"	79°18'38.82"	7.1	3.62	0.08
M24	12°56'41.83"	79°18'32.56"	7.0	<0.01	0.07
M25	12°56'53.21"	79°18'58.78"	6.8	<0.01	0.05

analyzed in Dr.M.G.R Educational Research Institute for different physico-chemical parameters such as P_H, Hexavalent chromium and total chromium as per standard procedures by Andrew and Arnold (1995) tabulated in Table 1 and 2. The quality of ground water been assessed by comparing each parameters with the standard desirable limit of that parameter in drinking water as prescribed by ISI 10500-91 and WHO standards in Table 1 and 2 (Hem, 1984).

RESULTS AND DISCUSSION

pH is one of the important parameter of water body since most of the aquatic organisms are adopted to an average pH. In this investigation, p_H values vary from 6.6-11 where as the pH value of drinking water is specified as 6.5-8.5 as per the standards prescribed by ISI 10500-91 and 7.0 TO 8.0 by World Health Organization (1993). The results indicate ground water source in the study area is alkaline in nature.

Oxidation form of chromium is hexavalent chromium which is highly toxic. This leads to lung and stomach cancer for humans. Based on the drill, hexavalent chromium was analyzed and the results were tabulated. In the present study hexavalent chromium was found below the permissible limit in most of the bore well samples. Higher contamination was noticed in 10 bore wells in and around the TCCL site of 2.25 km^2. The result shows higher concentration of 1.06-142.30 mg/L which is much above the prescribed limits of ISI 10500-91 and WHO standards.

Chromium 3 and 4 are covered under total chromium. Chromium 3 is nutritionally essential for human and is often added to vitamins. People who use water containing excess total chromium experience allergic dermatitis. In the present study total chromium found to be within allowable limit in most of the bore wells except 2 bore wells. The concentration of total chromium varies from 0.06-28.47 mg/L which is above the permissible limits of ISI 10500-91 and WHO standards (Fig. 3 and 5).

In the study 25 samples were collected as mentioned (Table 2) by boring wells to a depth of 4-5 m and as a result 9 samples were highly contaminated with hexavalent chromium. The graph has been plotted for all the 25 bore wells in an area of 42.3 km^2 and as a result, it has been concluded that only 2.25 km^2 of area are highly hexavalent chromium contaminated. The graph for the working area of 2.25 km^2 were plotted and the highly chromium contaminated bore wells were established and the stations are M5, M8, M9, M16, M17, M19, M20 M22 and M23. Figure 4 variations of hexavalent chromium and total chromium. With reference to the reports of NGRI-NEERI in 2005, 2007 and by this study in 2015, it is observed that about 2.25 km^2 area is beyond the permissible limits and are highly hexavalent chromium contaminated in and around the TCCL site and the remedial measures are to be performed only in the prescribed area. It has also been noted that the sample which were taken inside the TCCL is highly chromium contaminated (M8) and therefore, it is required to stop further seepage of hexavalent chromium towards the Palar river which is the main source of drinking water. Geo chemical fixation technology can be adopted by extracting contaminated ground water and treating it above ground followed by reinjection of the treated ground water into the aquifer (Todd, 2006). The reinjected ground water is dosed with a reductant to reduce any residual Cr^{6+} contamination to Cr (3). The success of this insitu treatment depends upon the ability of the applied reductant.

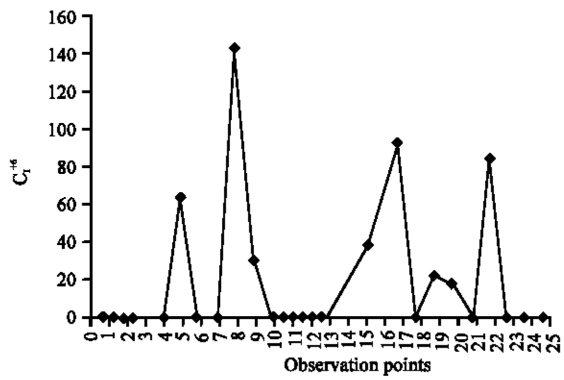

Fig. 3: Variations of hexavalent chromium

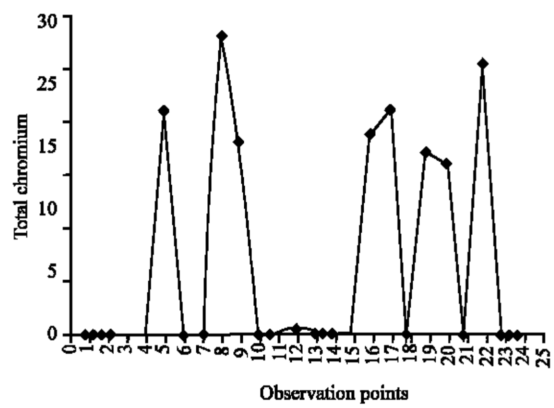

Fig. 4: Variations of total chromium

The total chromium concentration in the aquifer is not decreased but chromium is precipitated and fixed (immobilized) onto aquifer solids as Cr (3). In general, sulfur compounds such as sulfide and sulfite reduce Cr^{6+}. For sulfides to reduce Cr^{6+}, Fe (2) must be present to act as a catalyst. Thus, in aquifer systems where iron sulfides are present, reduction of Cr^{6+} may occur. However because the rate of reduction is slow, the iron sulfide reduction process may not effectively treat large volumes of water.

According to Palmer and Wittbrodt (1991), the following reactions occur. In the presence of excess sulfite, the reduction of Cr^{6+} follows the reaction. The metabisulfite ($S_2O_6^{-2}$) formed by the above reaction can then reduce oxidized Fe (3) to Fe (2), if it is present:

$$6H^+ + 2HCrO_4^- + 3HSO_3^-(\text{excess}) \rightarrow$$
$$2Cr^{+3} + 2SO4^{-2} + S_2O_6^{-2} + 6H_2O$$

This situation allows for potential reduction of Cr^{6+} by Fe (2). In the presence of excess Cr^{6+}, the reduction of Cr (3) by sulfite follows the reaction:

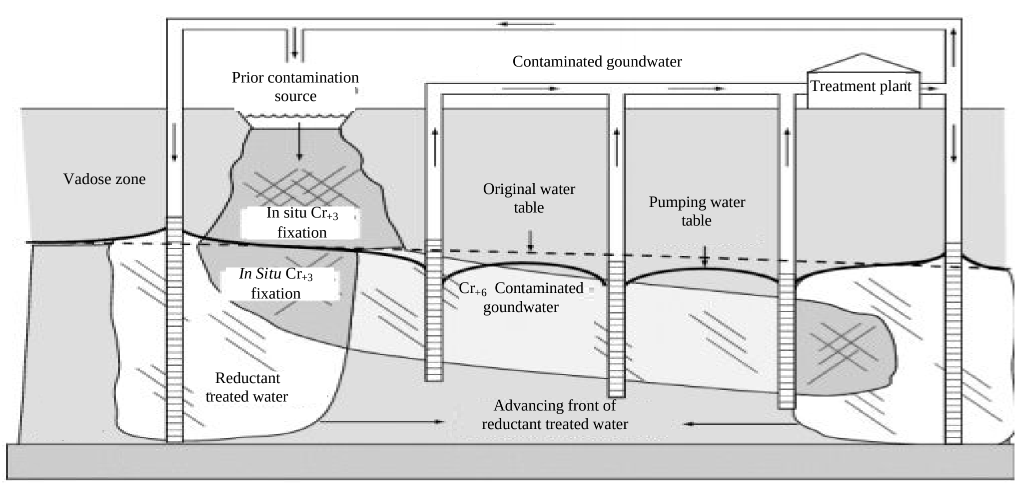

Fig. 5: Schematic diagram of in situ chromium remediation

$$5H^{+} + 2HCrO_4^{-}(\text{excess}) + 3HSO_3^{-} \rightarrow$$
$$2Cr^{+3} + 3SO4^{-2} + 5H_2O$$

Using this technology, groundwater is extracted, treated with a chemical reagent and reinjected along the contaminant plume perimeter (Fig. 4) as the treated water is directed towards the center of the plume, Cr^{6+} is reduced to Cr (3), its less soluble form. The zone of contamination is driven inward by the reaction front, leaving behind an increasingly larger clean water zone. Alternatively, injection can occur in the high concentration areas to effect a more rapid remediation (Brown *et al*., 1998). *In situ* geochemical fixation can be applied to source or core zones, the concentrated or active zone or the dilute or neutralized zone of the contaminant plume.

CONCLUSION

In order to restrict further seepage of hexavalent chromium towards the Palar River, construction of a wall on the downstream side of the TCCL site is found out as mandatory and the first measure is being suggested as by constructing an impermeable dyke.

The second aspect is to treat the ground water which is highly hexavalent chromium contaminated, till it reaches to the permissible limit in the zone which is of 2.25 km^2 of area. This can be achieved by many in-situ technologies but the suggested one is geochemical fixation method which will can be a long term remedial measure. The ultimate goal of the technology is to reduce hexavalent chromium Cr^{6+} which is highly toxic to the trivalent chromium Cr (3) as to be less toxic or no toxic sometimes.

Once the ground water treatment process is over there would need to dispose sludge which comes out as the by-product. Treatment of sludge in order to dispose and to make transportable to avoid environmental impact is found out as mandatory. In this context, the third measure is being suggested as TSDF which stands for treatment storage disposal facility. In this process the by-product generated in the form of sludge are taken for disposal generally in the dumping ground to avoid the environmental effects. The term treatment in this context can be defined as the process of changing the physical, chemical, biological character to make transportable as far as environmental factors are concerned. The three stages of remedial measures have been suggested taking the bench mark of TCCL site in SIPCOT complex. It can be concluded that the measures will prove easy, economic, environmental friendly and can be taken as long term remedial measure.

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