Jr. of Industrial Pollution Control 23 (2)(2007) pp 197-203

CHROMIUM : AS A POLLUANT

RISIKESH THAKUR, G.D. SHARMA, B.S. DWIVEDI AND S.K. KHATIK

Department of Soil Science and Agricultural Chemistry,
J. N. Krishi Vishwa Vidyalaya, Jabalpur 482 004, M.P., India

Key words : Chromium, Toxicity, Bioremediation, Chelation.

ABSTRACT

Contanimation of chromium is considered a serious environmental pollutant due to wide industrilization. The chromium concentration in plants 0.006 to 18 ppm and soil ranging from 10 to 50 ppm depending on parent material. Accourding to Environmental Protection Agency (EPA) < 0.1 ppm concentration of chromium in drinking water is permissible on the basis of health considerations. Toxicity of Cr to plants depends on its valence state Cr (VI) is highly toxic and mobile, where as Cr (III) is less toxic. Cr (VI) is present as either dichromate ($Cr_2O_7^{2-}$) in acidic environments or as chromate (CrO_4^{2-}) in alkaline environemts. Charomium toxicity affects the plant dry matter yield as well as some physiological processes such as photosynthesis, mineral nutrition etc. Remediation of soils contaminated with Cr using biorimediation, cheletion and remediation by reduction tecniques appears to have great potential for clean up of Cr – Contaminated sails and water.

INTRODUCTION

Chromium was first discovered in the Siberian red lead ore (crocoite) in 1798 by the French chemist Louis - Nicholas Vauquelin. Chromium is a greak word (Chroma = colour), which means coloured compounds. Due to wide industrial use, chromium is considered a serious environmental pollutant. Contamination of soil and water by chromium is of recent concern chromium occurs nature in bound forms that constitute 0.1 - 0.3 mg kg^{-1} of the Earth's Crust. A maximum acceptable concentration of 0.05 mg L^{-1} (50 mg L^{-1}) for chromium in drinking water has been establised on the basis of health considerations. Toxicity of chromium to plants depends on its valence state, Cr (VI) is highly toxic and mobile (which are usually occurs associated with oxygen as chromate (CrO_4^{2-}) or dicromate ($Cr_2O_7^{2-}$). Whereas, Cr (III) is less mobile, less toxic and is mainly found bound to organic matter in soil and aquatic environments (Becquer *et al.*, 2003). Chromium is a major source of aquatic pollution in India but the main aeras for their concentration are TamilNadu, Uttar Pradesh and West Bengal.

Position in the periodic table

Chromium (atomic number 24, atomic mass 51.99) has on outer electronic configuration of $3d^5$ $4S^1$ and belongs to VI B group or chromium group on the periodic table. In soil the ionic form of chromium that is observed by plants are Cr^{+3} and Cr^{+6}. Cr (III) was absorbed more rapidly then Cr (VI). The different oxidation state of chromium is given in below (Table 1).

Table 1
Different oxidation state of chromium and its compounds

S. No.	Chromium		
	Oxidation state	Electronic configration	Compounds
1.	O	(Ar) $4S^1$ $3d^5$	$Cr\ (Co)_6$
2.	+ 1 (Unstable)	(Ar) $3d^5$	-
3.	+ 2 (Chromus)	(Ar) $3d^4$	$Cr\ (CH_3COO)_4$, CrO, $CrSO_4$
4.	+ 3 (Crhomic) (Stable)	(Ar) $3d^3$	$CrCl_3$, Cr_2O_3, $Cr_2\ (SO_4)_3$
5.	+ 4 (Unstable)	(Ar) $3d^2$	CrO_2
6.	+ 5 (Unstable)	(Ar) $3d^1$	CrF_5
7.	+ 6 (Stable)	(Ar)	$K_2Cr_2O_7$, $K_2Cr_2O_4$, CrO_3

Note : Cr^{+3} are maximum stable, because it is not both oxidising and reducing agent.

Chromium in the environment

Chromium is found in all phases of the environment including air, water and soil (Table 2).

The chromium concentration in soil ranges from 10 to 50 mg kg^{-1} (Adriano, 1986). Cr concentration varies widely in the atomsphere from background concentration of 5.0×10^{-6} to 1.2×10^{-3} mg m^{-3} in air samples from remote areas such as Antarctica and Greenland to 0.015 to 0.03 mg m^{-3} in air samples collected over urban areas (Nriagu, 1988).

Anthropogenic source of chromium

Cr and its compounds have multifarious industrial uses. They are extensively employed in leather processing and finishing (Nriagu, 1988) in the production of refractory steel, drilling muds, electroplanting cleaning agents, and catalytic manufactur and in the production of chromic acid. Hexavalent chromium (VI) componds are used in industry for metal planting, cooling tower water treatment, hide tanning and until recently, wood preservation. These anthropo-

TABLE 2

Chromium concentrations in the environment

Sample type	Concentration
Natural soils	10 to 15 mg kg^{-1}
Serpentine soils	634-125,000 mg kg^{-1}
World soils	200 mg kg^{-1} (mean)
	100-300 mg kg^{-1}
	10-150 mg kg^{-1}
US soils	25-85 mg kg^{-1}
	57 mg kg^{-1}
Canadian soils	100-5000 mg kg^{-1}
Japanses soils	87 mg kg^{-1}
Swedish soils	74 mg kg^{-1}
Sediments	0-31,000 mg kg^{-1}
Fresh water	0-117 mg L^{-1}
Sea water	0-0.5 mg L^{-1}
Air	1-545,000 ng m^3
	100 ng m^3
Plants	0.006-18 mg kg^{-1}
Animals	0.03-1.6 mg kg^{-1}

TABLE 3

Concentration of chromium and other heavy metals in some typic igneous rocks and coal ash

S.No.	Trace elements (ppm)	Rock types		Coal ash	
		Granite	Basalt	Mean coal ash content	Crustal abundance
1.	Cr	9.0	16.03	246	100
2.	Cd	0.010	0.067	11	0.2
3.	Cu	10.7	22.4	217	55
4.	Ni	6.4	18.0	171	75
5.	Pb	28.7	18.0	287	13
6.	Zn	74.9	132.0	572	70

TABLE 4

Chromium concentration in selected fertilizers and soil amendments

S.No.	Fertilizers / soil amendments	Cr (ppm)	Reference
1.	Rock phosphate	33.2 to 140	Reven and Loeppert, 1997
2.	Tripal super phosphate	88.9	Reven and Loeppert, 1997
3.	Poultry manure	<1.1 to 7.7	Wolfgang and Dohler, 1995
4.	Swine manure	1.3 to 2.2	Wolfgang and Dohler, 1995
5.	Municipal waste	7.6	Heckman and Kluchinski, 1996
6.	Sewage – slugde	26.0	NJDEP, 1999

genic activities have led to the wide spread contamination that Cr shows in the environment and have increased its bioavailability and biomobility. (Kotas and Stasicka, 2000).

The leather industry is the major cause for the high influx of Cr to the biosphere, accounting for 40% of the total industrial use (Barnhart, 1997). In India, about 2000 to 32000 tons of elemental Cr annually escape into the environment from tanning industries. Even if the recommonded limit for Cr concentration in water are set differently for Cr (III) (8 mg L^{-1}) and Cr (VI) (1 mg L^{-1}), it ranges from 2 to 5 g L^{-1} in the efluents of these industries (Chandra *et al.* 1997).

The chromium content as well as other heavy metals in any soil depends initially on the nature of parent materials. Flanagan (1969) reported that the concentration of heavy matels was higher in basaltic rocks and comparatively low in granite rocks and Vine and Tourlets (1970) reported that the heavy metal composition in coal ash (Table 3). Some fertilizers and soil amendments also contain chromium in soil (Table 4).

Uptake of chromium

Chromium is a toxic, non-essential element to plants, hence they do not posses specifric mechanisms for its uptake. Therefore, the uptake of this heavy metal in through carriers used for the uptake of essential metals for plant metabolism. The pathway of Cr (VI) transport is an active mechanism involving carriers of essential anions such as sulphate (Cervantes *et al.* 2001). Fe, S and P are known also to complete with Cr for carrier binding (Wallance *et al.* 1976).

Independent uptake mechanisms for Cr (VI) and Cr (III) have been reported in barley. The use of metabolic inhibitors diminished Cr (VI) uptake whereas it did not affect Cr (III) uptake, indicating that Cr (VI) uptake depends on metabolic energy (Skeffington *et al.* 1976). An active uptake of both Cr species, slightly higher for Cr (III) than for Cr (VI), was found in the same crop (Ramachandran *et al.* 1980).

Chromium toxicity in plants

Toxicity of Cr to plants depends on its valence state, Cr (VI) is highly toxic and mobile whereas Cr (III) is less toxic. Toxic effects of Cr on plant growth and development include altrations in the germination process as well as in the growth of roots, stems and leaves, which may affect total dry matter production and yield. Cr also causes deleterious effects of plant physiological processes such as photosynthesis, water relation and minerals nutrition.

In plans, high levels of Cr supply can inhibit seed germination and subsequent seedling growth. Peralta *et al.*, (2001) found that 40 ppm of Cr (VI) reduced by 23% the ability of seeds of lucerne (*Medicago sativa*) to germinate and grow in the contaminated medium. Reductions of 32-57% in sugarcane bud germination were observed with 20 & 80 ppm Cr, respectively (Jain *et al.* 2000).

Remediation of chromium contaminated soils and water

Chromium remendiation through microorganism or plants may be the best technology in preset to clean up Cr contaminated sites. Yadav *et al.* (2005) gives some remediation process for Cr contaminated soil and water which are given below :

1. Bioremediation : The decontamination of polluted or degraded soils by means of enhancing the chemical degradiation or other activity of soil organisms. Losi *et al.* (1994), they found that organic matter content, bioactivity and oxygen status were among the important factors. Under aerobic field moist condiations, organic matter rich soil reduced 96% of added Cr (VI). Organic matter enhances the reduction of chromate in soil by increasing microbial activities. Bacterial populations resistant to as much as 500 mg L^{-1} Cr (VI) were directly isolated from two uncontaminated soils.

2. Phytoremediation : Phytoremediation of Cr pollution can be achieved by using plants to remediate heavey metal contraminated sites called phytoremediation. Shahandesh and Hossner (2002) reported that the *Brassica junea* and *Helianthus annus* plant speices absorbed maximum Cr concentration about 1400 mg kg^{-1}.

3. Rhizofiltration : Another promising clean up technology appears to be rhizofiltration which involves use of plant roots to remove contaminants such as heavy metals from contaminated water (Dushenkov *et al.* 1995). Generally aquatic plants are growing in contaminated water. Examples- *Scirpus lecusteris, Phragmites karka* and *Bacopa monnieri.*

4. Phytoextraction : The extraction of metal from polluted soils into harvestable plant tissues (Phytoextraction). Very few plant species such as *Sutera fodina, Dicoma niccolifera* and *Leptospermum Scoparium* have been reported to accumulate Cr to high concentrations in their tissues.

5. Cheletion : Nutrient culture studies revealed a marked enhancement in uptake and translocation of chelated ^{51}Cr in *P. verlgaris*. Cr chelated by DTPA was most effectively translocated followed by ^{51}Cr-EDTA and ^{51}Cr-EDDHA (Alhalyc *et al.* 1995).

6. Remediation by reduction of Cr (VI) in soils : Remediantion by reduction schemes employing microbiological and chemcial processes. Many new techniques and chemical reaction have been developed for the remediation of Cr (VI) - contaminat soils and ground water including those using carbon based minerals, zero and divalent Fe, reduced sulphur containing compounds and H_2 gas. The rates and extent of reduction of Cr (VI) by each of these are dependent on pH, aeration status and the concentration and reactivity of the reducing agent.

Manures have been used successfully to reduce Cr (VI) in chromite ore processing, residue - enriched soils (Higgins *et al.* 1997). Zero valent Fe has been especially with reactive permeable barrier walls (Puls *et al.* 1999) and divalent Fe has been used for reduction of Cr (VI) in soil and aqueous systems, with Fe (II) in soluble and insoluble forms and with and without light indused reduction of Fe (III), (Buerge and Hug, 1999). Reduced sulphur containing compounds (eg. Fe (II) sulfides, dithionite etc) have been used to reduce Cr (VI) directly or to creat reduced colloids or conditions in soils and ground water, (Zouboulis *et al.* 1995). Hydrogen gas has also been used to reduce Cr (VI) under methanogenic conditions, (Marsh and McInerney, 2001).

CONCLUSION

Chromium is a metal found in nature deposites. The two largest sources of chromium emission in the atmosphere are from the chemical manufacturing industry and combustion of natural gas, oil and coal. The greatest use of Cr is in metal allooys such as stainless steel, protective coatings on metal, magnetic tapes and pigments for paints, cements, paper etc.

According to EPA found Cr to potenially cause the following health effects when people are exposed to it at levels skin irritation or ulcreation, damage to liver, kidney, circulatory and nerve tissues. If the Cr (VI) compounds present in high concentration can increase the risk of lung cancer.

Chromium bioremediation through microorganism or plants may be best technology in present to clean up Cr contaminated sites and these technologies are eco feiendly.

REFERENCES

Adriano, D.C. 1986. Trace elements in the trrestrial environment. New York : Springer verlag. 105-23.

Athalye, V.V., Ramachandarn, V. and D'Souza T.J. 1995. Influence of chelating agents on plant uptake of ^{51}Cr, ^{210}Pb and ^{201}Po. *Envoron. Pollut.* 89 : 47-53.

Barnhart, J. 1997. Occurrences, uses and properties of chromium. Regul Toxicol Pharm, 26 : 53-57.

Becquer, T., Quantin, C., Sicot M. and Boudot, J.P. 2003. Chromium availbility in ultramafic soils from New Caledonia. *Sci. Total Environ.* 301 : 251-61.

Buerge, I.J. and Hug, S.J. (1999). Influence of mineral surfaces on chromium (VI) reduction by iron (II). *Environ. Sci. Technol.* 33 : 4285-4291.

Cervantes C., Garcia, J.C., Devars, S., Corona, F.G., Tavera, H.L. and Torres-guzaman Carlos, J. 2001. Interactions of chromium with micro-organisms and plants. *FEMS Microbial. Rev.* 25 : 335-47.

Chandra, P., Sinha, S. and Rai, U.N. 1997. Bioremediation of Cr. from water and soil by vascular aquatic plants. *ACS Sympopsium*, series, vol. 664, Washington, p. 274-282.

Dushenkov, V., Kumar, P.B.A.N., Motto, H. and Raskin, I. 1995. Rhizoflitration : the use of plants to remove heavy metals from aqueous stream. *Environ. Sci. Technol.* 29 : 1239-1245.

Flanagan, F.S. 1969. Geochim cosmochi *Acta.* 33 : 81-120.

Heckman, R.J. and Kluchinski, 1996. Chemical composition of municipal leaf waste and hand collected leaf Litter. *J. Environ. Qual.* 25 : 355-362.

Higgins, T.E., Halloran, A.R., Petura, J.C. 1997. Traditional and innovative treatment methods for Cr (VI) in soil. *J. Soil Contamination.* 6 : 767-797.

Jain, R., Srivastava, S. and Madan, V. K. 2000. Influence of chromium on growth and cell division of sugarcane. *Indian J. Plant Physiol.* 5 : 228-31.

Kotas, J. and Stasicka, Z. 2000. Commentary : chromium occurance in the enviroment and methods of its speciation. Environ. Pollut, 107 : 263-83.

Marsh, T.L. and McIenerney M.J. (2001). Relationship of hydrogen bioavailability to chromate reduction in aquifer sediments. *Appl. Environ. Microbiol.* 67 : 1517-1521.

NJDEP 1999. Data summarized from 1997. Sludge quality assurance reported. (SQAR) 31 NJR. 202.

Nriagu, J.O. 1988. Production and uses of chromium. *Chromium in Natural and Human Environment.* New York, USA : John Wiley and Sons, p. 81-105.

Peralta, J.R., Gardea, Torresdey, J.L., Tiemann, K.J., Gomez, E., Arteaga, S. and Rascon,

E. 2001. Uptake and effects of five heavy metals on seed germination and plant growth in alfalfa (*Medicago sativa*) L. *B Environ. Contam Toxicol.* 66 (6) : 727-34.

Puls, R.W., Blowes, D.W. and Gillham, R.W. 1999. Long-term performance monitoring for a permeable reactive barrier at the US Coast Guard Support, Center, Elizabeth City, North Carolina. *J. Haz. Mat.* 68 : 109-124.

Ramachandra, V., D'Souza, T.J. and Mistry, K.B. 1980. Uptake and transport of chromium in plants. *J. Nucl. Agric. Biol.* 9 : 126-9.

Raven, K.P. and Loepppert, R.H. 1997. Trace element composition of fertilizers and soil amendments. *J. Environ. Qual.* 26 : 551-557.

Shahandeh, H. and Hossner, L.R. 2002. Plant Screening for chromium phytoremediation. *International Journal of Phytoremediation.* 2 : 31-51.

Skeffington, R.A., Shewry, P.R. and Petersen, P.J. 1976. Chromium uptake and transport in barley seedlings *Hordeum vulgare. Planta.* 132 : 209-14.

Vine, J.D. and Tourlet, E.B. (1970). Eco. Ecology, 65 : 253-272.

Wallace, A., Soufi, S.M., Cha, J.W. and Romney, E.M. 1976. Some effects of chromium toxicity on bush bean plants grown in soil. *Plant Soil.* 44 : 471-3.

Wolfgang, W. and Dohler, H. 1995. Schwermetalle in der landirschaft (Heavy metals in agri.). Kuratorium for technik. and Bauwesen in der landwisrschfte. V., Dramstadt. Garmany.

Yadav, Sumit, Shukla, O.P. and Rai, U.N. 2005. Chromium pollution and bioremediation, National Botanical Research Institute, Lucknow.

Zouboulis A.I., Kydros, K.A. and Matis K.A. 1995. Removal of hexavalent chromium anions from solutions by pyrite fines. *Wat. Res.* 29 : 1755-1760.