IUE - 4: ASSESSMENT FOR CHROMIUM CONTAINING WASTE FROM THE LEATHER INDUSTRY

2008 Updated document

Chromium (III) is the most widely used tanning agent in the leather industry; chromium(VI), the carcinogenic form, is not used in the tanning process. Chromium may be considered as a source of pollution due to the large volume of exhausted residual tanning floats and solid waste produced.

Cleaner technologies used to reduce chromium in wastewater, such as high exhaustion process, direct or indirect chromium recycling, cannot eliminate chromium from effluent completely, because there is typically significant discharge from post tanning. In addition, some chromium remains in sludge derived from tanning.

Total replacement of chromium has been attempted using combinations of metallic cations, for example titanium(IV), aluminium(III) and zirconium(IV), but the results obtained could not match chromium, in physical properties and character, but most importantly in hydrothermal stability. This makes such tannages unsatisfactory for most types of leather. Other options that have been proposed are: hydrolysable vegetable tannins, alone or in combination with a metal salt (semi metal tanning), condensed vegetable tannins, alone or in combination with an aldehydic crosslinker, synthetic organic tanning agents, alone or in combination with an aldehydic crosslinker. These traditional or new tannages can be used for some leathers, but none is suitable for all leather, like chrome.

Although apparently more ecologically acceptable, because they are derived from a natural, renewable resource, vegetable tanning cannot be considered more environmentally friendly than chrome tanning, due to the high pollution load and low treatability in conventional systems. Also vegetable tanned leather has different physical properties and limited modern applications. Vegetable tanned leather is less easily biodegraded than chrome leather. In both cases, the leather resists microbial attack, which is part of the definition of tanning. However, if the leather is damaged, chemically or thermally, it becomes vulnerable to enzymatic breakdown. In the case of chrome leather, it can be degraded with ease, because the tanning agent is completely bound to the collagen by the action of tanning. In the case of vegetable tanned leather, the tannins are weakly bound to collagen and are unaffected by chemical or thermal damage. Therefore, the tannins remain active, capable of interacting with attacking enzymes and deactivating their action: this makes vegetable tanned leather much more resistant to biological degradation.

Although chromium is an essential trace element for human health (glucose tolerance factor) (Iyengar 1989; Anderson 1989), there is no doubt that Cr(VI) compounds are both acutely and chronically toxic (Rinehart, 1989).

Cr(III) is less toxic than many other elements (Hg, Cd, Pb, Ni, Zn) to mammalian and aquatic organism, probably due to the low solubility of this element in its trivalent form at pH>4 (Moore and Ramamoorthy, 1984). Similarly, Cr(III) compounds also have a very low mobility in soils and are thus relatively unavailable to plants (Adriano, 1986).

Compared to Cr(VI), the toxicity of Cr(III) (chromium sulphate) is insignificant. Some toxicity levels of chromium sulphate in neutral medium (that is to say chromium salts used in the tannery) are shown in the following table (Carré and all., 1983).

	Cr(III) (mg/l)	**Cr(VI) (mg/l)**
Algae (*Scenedesmus subspicatus*) CIG 50, 5 days	> solubility	0.42
Bacteria (*Enterobacter aerogenes*) CIG 50, 8±1 hours	> solubility	6.4
Bacteria (*Pseudomonas fluorescens*) IC 99.9 %, 4 hours	> solubility	250
Urban activated sludge IC 50, 3±1 hours	75 *	5.3
Daphnia (*Daphnia magna Strauss*) IC 50, 24 hours	7.5 - 9	0.4
Fish (*Brachydanio rerio*) IC 50, 24 hours	> solubility	95

* For $CrCl_3$ (Semsari and Gaid, 1993)

Note:

CIG - Concentration level Inhibiting Growth

IC - Inhibitory Concentration

The reducing characteristics of tannery sludge stabilise Cr(III) with respect to Cr(VI), due to the presence of organic matter and sulphide (Adriano,1986; Losi and Frankenberger, 1993). Field investigations concerning Cr migration in soils treated with tannery sludge (Dreiss, 1986) have demonstrated low Cr(III) mobility.

Conventional incineration of sludge (with or without leather waste), although technically feasible, has limited application due to associated environmental problems (air pollution and possibility of chromium oxidation). Incineration at elevated pH (9-10), in the presence of an excess of oxygen, can lead to conversion of Cr(III) to Cr(VI). However, newer methods allow thermal treatment of materials containing Cr(III), including sludge, without forming Cr(VI).

In 1994, the US EPA case in the United States Court of Appeal for the District of Columbia failed, because they could not prove that trivalent chrome in sludge is damaging to the environment. It is believed by the IUE Commission that for an integrated tannery, operating from raw hide to wet blue, the lowest practical chromium level is 5000 mg Cr(III) per kg dry solids in the mixed tannery sludge, which is achievable using the best available practices and cleanest technologies. In 2003, the Indian government decided to follow the IUE guideline on certain aspects. It is suggested that particular attention should be given to the application loading of chromium on the land and not the concentration of chromium in the sludge. In 2000, the European Commission decided not to add chromium-containing waste to the hazardous waste list (Decision 2000/573, July 23rd).

In some countries the concentration of Cr (III) per kg dry solids in sludge is limited for application to edible crops (ranging from 5000 to 100 mg Cr(III) per kg dry solids).

To obtain a level lower than 1000 mg Cr (III) per kg dry solids, it is necessary to process separately chromium containing effluents such as residual tanning floats and post-tanning floats.

The Commission will follow any new results in the field of utilisation of chromium containing sludge and will update this document accordingly.

IUE Commission

October 2008

Bibliography

Adriano D. C. (1986) Chromium. In Trace elements in the terrestrial environment, pp. 58-76. Springer, New York.

Anderson R. A. (1989) Essentiality of chromium in humans. Sci.Total Envir. 86, 75-81.

Carré M. C., Vulliermet A., Vulliermet B. (1983) Environment and Tannery, p 92. CTC, Lyon.

Dreiss S. J. (1986) Chromium migration through sludge treated soils. Ground Wat. 24, 312-321.

Iyengar G. V. (1989) Nutritional chemistry of chromium. Sci.Total Envir. 86, 69-74.

Losi M. E. and Frankenberger W. T. (1993) Chromium resistant microorganisms from evaporation pond of a metal processing plant. Water, Air and Soil Pollution, 74, 405-413.

Moore J. W. and Ramamoorthy S. (1984) Chromium. In Heavy metals in natural waters (Edited by De Santo R. S.), pp. 58-76. Springer, New York.

Rinehart W. E. (1989) Recapitulation. Sci.Total Envir. 86, 191-193.

Semsari S. and Gaid A. (1993) Inhibition of chromium III on the activated sludge activity, Envir. Technol. 15, 255-262.

Senior K. (2000) Chromium in the leather industry. World Leather 13(7), 51-55.