

Boron in hide and skin curing processes

R A Rowswell, former UNIDO consultant



While reading through a review paper recently entitled 'Recent Progress in Cleaner Preservation of Hides and Skins', two references jogged my memory regarding the development of the LIRI-cure hide skin curing process. One, the mention of the LIRI-cure work done by Dr A E Russell, and the other, the use of sodium chloride and boric acid as short- to medium-term low-salt curing processes.

During the 1980s when LIRI (Leather Industries Research Institute) was in the process of developing the salt-free LIRI-cure process, boric acid (H_3BO_3) was used in its formulation. Once the cure had developed to the stage where field trials were conducted, LIRI-cured hides were sent to and processed by a wet blue tannery for industrial-scale tanning trials.

This wet blue tannery, which previously processed salt cured hides, was irrigating its treated effluents and treated sewage water to reduce the SAR (Sodium Absorption Ratio) of the tannery effluents to less than 9 for the particular soil type being irrigated, under the guidance of the Department of Water Affairs (DWA) and the Soil Irrigation Research Institute (SIRI).

Either Dr Thompson of SIRI or Dr W Fowler of the LIRI Analytical Laboratories, who previously worked for the Pineapple Research Institute, brought the issue of the toxicity of boron in irrigation waters to certain crops to our attention. The tannery and LIRI were fortunate that this issue was raised so early and LIRI consequently stopped using boron in its

short- to medium-term chemical cures.

In the Food and Agriculture Organization (FAO) of the UN's paper 'Irrigation and Drainage Paper No. 29' by R S Ayers and D W Westcott (1976), the toxicity and inhibitory effects of chloride, sodium and boron are discussed in detail for certain crops grown under irrigation with effluents containing these substances in excess of recommended concentrations.

The authors of the paper state: "Although BA (boric acid) does not pose any serious health or safety problems on usage, its use for curing has recently come under effluent restriction in some countries including Australia." It should be mentioned that these effluent restrictions are applied in South Africa and should be applied internationally.

Some information abstracted from the Irrigation and Drainage Paper No. 29 which is of relevance can be seen in Table 1.

Table 1: Guidelines for interpretation of water quality for irrigation

Irrigation problem	Degree of problem		
	No problem	Increasing problem	Severe problem
Salinity			
EC_w (mmhos/cm)	<0.75	0.75-3.0	>3.0
(mS/m)	<750	750 - 3000	>3000
Specific ion toxicity			
Sodium ^(1,2) (SAR)	<3	3-9	>9
Chloride ^(1,2) (meq/l)	<4	4-10	>10
Boron (mg/l)	0.75	0.75-2.0	>2.0

Note: EC_w – Electrical Conductivity of irrigation water
mmhos/cm $\times$ 640 = mg/l
mmhos/cm $\approx$ S/cm

- Most tree crops and woody ornamentals are sensitive to sodium and chloride.
- With sprinkler irrigation on sensitive crops, sodium or chloride in excess of 3meq/l, under certain conditions, has resulted in excessive leaf absorption and crop damage.

Table 2: Recommended maximum concentrations of trace elements in irrigation waters

Element (symbol)	For waters used continuously on all soils mg/l	For use up to 20 years on fine textured soils of pH 6.0 to 8.5
Aluminium (Al)	5.0	20.0
Arsenic (As)	0.1	2.0
Beryllium (Be)	0.1	0.5
Boron (B)	*	2.0
Cadmium (Cd)	0.01	0.05
Chromium (Cr)	0.1	1.0
Cobalt (Co)	0.05	5.0
Copper (Cu)	0.2	5.0
Fluoride (F)	1.0	15.0
Iron (Fe)	5.0	20.0
Lead (Pb)	5.0	10.0
Lithium (Li)**	2.5	2.5
Manganese (Mn)	0.2	10.0
Molybdenum (Mo)	0.01	0.5***
Nickel (Ni)	0.2	2.0
Selenium (Se)	0.02	0.02
Vanadium (V)	0.1	1.0
Zinc (Zn)	2.0	10.0

These levels will normally not adversely affect plants or soils

* See Table 1

** Recommended maximum concentrations for irrigating citrus is 0.075mg/l

*** For only acid fine textured soils or acid soils with relatively high iron oxide contents

Source: Environmental Studies Board, Nat. Acad. of Sci., Nat. Acad. of Eng. Water Quality Criteria, 1972.



The current trend in the hide and skin processing industry is to avoid, where possible, substances that are detrimental to the environment and it is felt that in these reviews a strong cautionary note should be included when mentioning processes that are detrimental to the environment in any way (e.g. not advised where effluent is used for irrigation). After all, that is why processes are being developed to avoid the use of sodium chloride in processing.

Boron is a necessary micronutrient for plant growth. However, if excessive, boron becomes toxic. A boron toxicity problem is usually associated with boron in the irrigation water as opposed to the ground water. The sensitivity to boron appears to affect a wide variety of crops, while sodium and chloride toxicities were mostly centred on tree crops [fruit] and woody perennials.

From perusing the literature available internationally, it is evident that tannery effluents are widely used for irrigation purposes. Table 3, which appeared in Water Treatment Handbook by Gilbert Degremont, early edition, should be of assistance.

Although this article was initially intended to alert the hide and skin processing industry to the dangers of using curing processes which include boron in any form where treated wastewaters are used for irrigation, it is felt that other important issues with respect to using tannery effluent for irrigation purposes also warrant mention.

As LIRI's Environmental Division was involved in advising the tannery on improvements to its wastewater treatment process it was decided by the company's management that, as it was more technically skilled, it was in a better position to assist with the irrigation in regard to monitoring and communication with the relevant government department (DWA) and research institute (SIRI).

In 1984, an independent assessment was carried out by the Rhodes University Hydrological Research Unit on the feasibility of using wet blue tannery effluent for irrigation. At the time, tannery effluent was applied by spray irrigation followed by an application of treated sewage water. This practice was found to be counterproductive as the high SAR (± 40) of the tannery effluent resulted in the hydraulic failure of the soil and the subsequent application of

Table 3: Criteria for classification of irrigation water

Classes	Na ⁺ x 100 Na ⁺ + K ⁺ + Mg ⁺ + Ca ⁺	Dissolved Solids (mg/l)	Boron (mg/l)	Chlorides (mg/l)	Sulphates (mg/l)
Class I: Water excellent to good, suitable for most plants in majority of cases	0 - 60	0 - 700	0 - 0.5	0 - 177	0 - 960
Class II: Water good to poor, harmful for some plants in some soil, climate and cultivation conditions	60 - 75	700 - 2100	0.5 - 2	117 - 355	960 - 1920
Class III: Water poor to unusable, not suitable in most cases	75+	2100+	2+	355+	1920+

Note: Irrigation water must above all be free from toxic or radioactive substances, hydrocarbons and greases.

Excess salinity destroys the structure of the soil. Some products may impair the taste of certain vegetables and fruits. On the other hand, the presence of certain organic content may have nutrient value for the plants
Source: Water Resources of California – Bull. I, Sacramento (1951)

sewage water was unable to infiltrate the soil, thus obviating any possible dilution effect. The report also pointed out that the sulphate content of the soil solution is greater than the chloride content, a feature generally uncommon in the irrigated soils of South Africa. High concentrations of SO₄⁼ in the presence of Ca⁺⁺ will, once the Ksp (Solubility Product) is exceeded, invariably lead to gypsum precipitation. By blocking

existing soil pores, this latter process will further decrease the permeability of the soil. (Moolman, 1984).

A special short-term concession was given to the tannery in November 1984 to process a proportion of wet salted hides due to the drought and the shortage of chemically cured hides.

This short-term concession was rescinded in April 1986.

In 1985, a directive was issued that

Table 4: Improvements in tannery effluent quality

Determinations	Before improvements to WWT plant (Prior to 1984)	After aeration tank and clarifier installed (1985 - 1986)	After pre-treatment, chrome recycle and recovery installed (1987 - 1988)	Sewage effluent (1987 - 1991)
	(Average of 3 samples)	(Average of 9 samples)	(Average of 8 samples)	(Average of 23 samples)
pH	8.4	7.03	6.41 (6.24)*	6.86
EC (S/m)	-	2.45	1.51 (1.39)	70.9
TDS (%)	2.70	2.45	1.45 (1.39)	419
TDIS (%)	1.63	1.91	1.02 (0.97)	280
COD (mg/l)	20020	28514	8784 (3354)	159
SS (mg/l)	8900	5240	510 (193)	20
Sulphide as S (mg/l)	314	296	83 (17)	-
Chrome as Cr (mg/l)	560	264	7 (<1)	-
SAR		39.6**	16.0***	2.9

* Figures in brackets are the mean values of the more recent analyses (Sept 1987 to July 1988). The improvements result from better management and the settling down of the wastewater treatment plant after commissioning.

** From an average of 25 effluent samples taken in August and September 1986

*** The mean SAR of treated tannery effluent corresponding to the average sewage effluent parameters and period of monitoring.

the tannery effluent and the sewage water should be mixed prior to irrigation so that the combined irrigation water had an EC <500, pH between 5 and 9, sodium absorption ratio (SAR) <9 and chrome <4mg/l.

From May 1985 the tannery was restricted to processing only chemical cured hides by the DWA. Although, a minimum of salt (NaCl) was used in the curing process, salts from the pickling process were present in the final wastewater and could have had an effect on the permeability of the soil. The tannery acquired the services of Dr J G Thompson of the SIRI to advise on remedial action to be taken regarding the practicalities of this irrigation practice. It was advised that gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) be applied to the soil to improve permeability. This was later changed to phosphor-gypsum as tannery effluent has a very low phosphate content.

In 1986, LIRI advised the tannery on the possibility of reducing the quantities of certain specific chemicals used in their processing recipe, which would have a beneficial effect on the SAR value of their treated effluent. In 1987, a chrome recycling and recovery plant was commissioned. As a result of improvements to the wastewater treatment system, better management and reduced chemical use in processing, improved tannery effluent quality was achieved (Table 4).

From Table 4 it can be seen that the SAR values of 1986 required an approximate dilution with treated sewage water of 12 times, while from 1987 onwards this was reduced to approximately four times to achieve a combined SAR of <9.

The following are important factors to consider when contemplating irrigation with tannery effluent:

- The chemical composition of both the tannery and diluting effluents must be determined: SAR, pH, EC and TDS. The tables of this article will give an indication of the analyses to be undertaken.
- The soil type where the irrigation is to take place must be established. This must be done by a soil irrigation specialist.
- The irrigation application rate (Kilolitre/Ha) must be determined.
- Ongoing monitoring of irrigation water and soil by chemical analysis.
- The irrigation area should not be close to a water course where potential runoff and/or seepage can affect the water quality.
- Monitoring of the subterranean water quality should also be undertaken. ☼

References

R S Ayers and D W Westcott (1976), *Irrigation and Drainage Paper No. 29, Water Quality for Agriculture, Food and Agriculture Organization of the United Nations, Rome.*

Moolman, J H (1984), *A preliminary feasibility study on the use of tannery effluent for irrigation purposes – Report to Leather Industries Research Institute, Hydrological Research Unit, Geography Department, Rhodes University, Grahamstown, RSA.*



Die Chemie stimmt [Ⓢ]

Simply good chemistry [Ⓢ]

Creamos buena química [Ⓢ]

La chimie à l'écoute de vos besoins [Ⓢ]

Creiamo buona chimica [Ⓢ]

A Química Certa [Ⓢ]

我们天生对味 [Ⓢ]

www.trumpler.com

 **150 years**
simply good chemistry