

Oxidation and Precipitation 1995

Like many processes, leather manufacture creates effluent: solid, liquid and gaseous byproducts - waste.

Despite intensive action by the industry resulting in a substantial reduction of environmental pollution, increasingly stringent legislation has been introduced in the wake of an enhanced awareness of environmental problems.

In Germany, the Water Resources Policy Act has laid down requirements concerning the introduction of effluent into waterways. Separate effluent streams containing hazardous materials is one area subject to these regulations.

For effluent originating from the leather process the sulphide and chrome containing effluent stream, together with the various post tanning liquors must be pretreated. This is also the case for indirect discharge, ie before discharge into the public System.

The limiting values have been defined as 2 mg/l (ppm) for sulphide and 1 mg/l (ppm) for total chrome.

The principle of separate treatment is intended to remove the hazardous substances from the waste water as early as possible so avoiding contamination of greater volumes of effluent and the resulting sludge.

In the event of joint treatment it is necessary to achieve the same level of contaminant reduction as when using separate treatment processes.

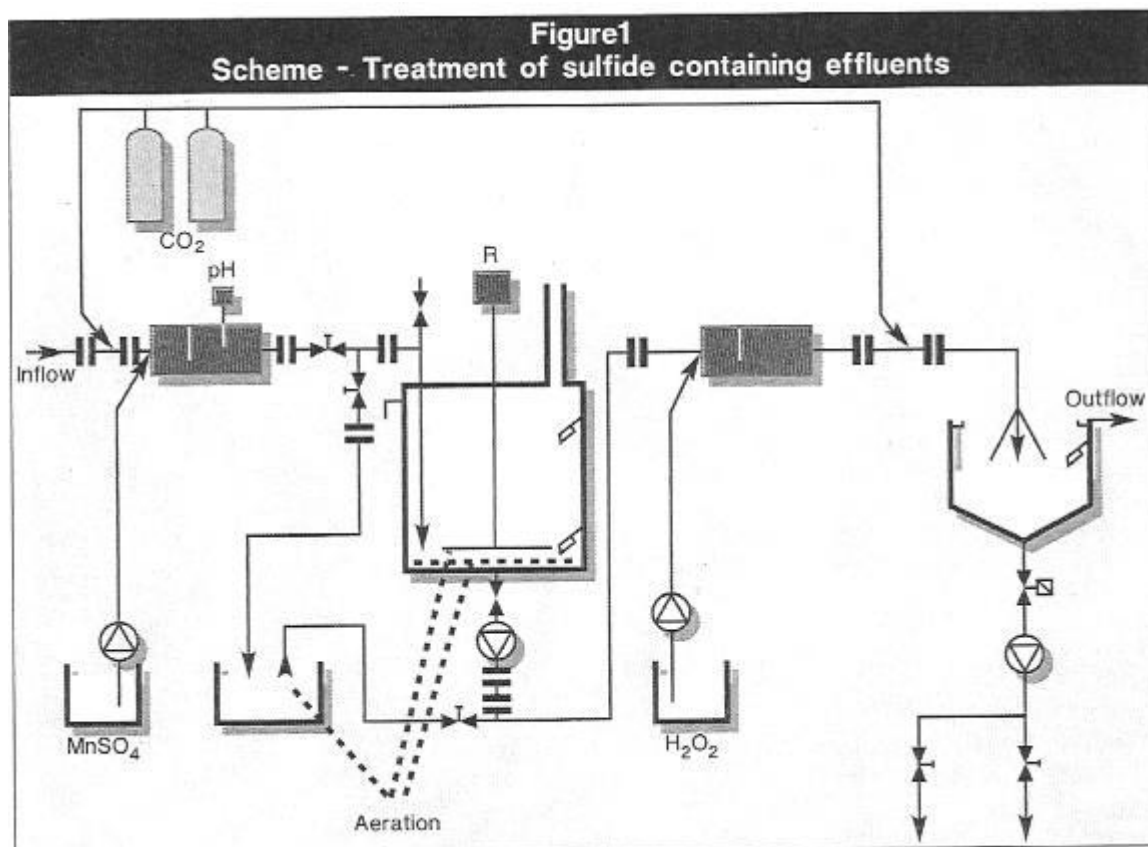
For tanneries which are not able to operate their own sewage plant complete with biological purification stage, it is, therefore, ideal for effluents containing sulphide and chrome to be channelled immediately into separate systems.

Table 1:

Table 1 Sulfide oxidation by aeration				
Aeration	Air [Nm ³ /h]	Sulfide concentration start [mg/l]	7h [mg/l]	24h [mg/l]
via membranes	12	462	147	3
	22	269	4	2
	44	462	5	3
	44	284	6	2
	44	231	2	
Via stirrer	(3 bar)	377	196	2
	(6 bar)	348	21	2

Mn²⁺ - concentration = 50 mg/l in all trials

Figure 1:



The stream containing sulphide can be treated either:

- by precipitation using iron (II) salts or
- oxidation using suitable reagents

As the precipitation process produces a high sludge volume which must be dewatered before disposal, and as the landfill Space is now at a premium and expensive, oxidation of the effluent by atmospheric oxygen was investigated.

Previous research at the WGR using a loop reactor ascertained the importance of manga-nese (II) salts as a catalyst to the sulphide oxidation process. Without the manganese the process is extremely slow.

After a rapid reduction of the sulphide concentration, from 800 mg/l down to 10-40 mg/l in one hour, a reduction to 5 to 10 mg/l was noted following a further six hour aeration.

In order to comply with the required set limit of 2mg/l it is necesaary to add hydrogen peroxide as an additional oxidising agent before releasing the effluent.

Table 2:

Table 2 Precipitation of Cr in different floats (with magnesium oxide)						
	COD [mg/l]	Cr [mg/l]	pH	sludge vol. after 24h [ml/l]	Cr filtered [mg/l]	Cr unfiltered [mg/l]
Cr tanning	2172	2789.0	9.1	70.0	0.9	4.9
sammying	2898	1221.0	9.1	26.0	3.9	9.9
washing	225	65.8	9.1	1.0	1.7	12.6
neutralisation	1932	15.2	9.1	3.0	0.9	2.4
dyeing	786	7.2	9.1	14.0	0.3	1.2
dyeing + fatliquor	2314	10.5	8.6	0.3	9.4	9.6
dyeing + fatliquor + retanning	9249	19.8	8.7	85.0	8.3	10.5
washing	1882	9.1	8.9	13.0	4.3	7.1

The use of H_2O_2 alone cannot be considered for reasons of cost. Also, it reacts with other substances present in the effluent so that stoichiometric application with regard to the sulphide content is by no means guaranteed.

Trials suggest that with a residual sulphide content of 10 mg/l, approximately 0.5 litres/ m^3 hydrogen peroxide needs to be added.

Figure 1 shows a scheme for sulphide treatment. An aeration tank, 4.5 metres high, 15 m^3 capacity, effects the aeration by means of jets in the agitator blades.

As experiments had shown that oxidation took place more quickly in less alkaline conditions the plant allows for a reduction in pH using CO_2 . It is also possible to meter the addition of hydrogen peroxide.

During experiments in which the catalyst application was varied between 50 and 200 mg/l of Mn(II), a 24 hour aeration period was necessary in order to reach the limiting value of 2mg/l. The initial sulphide concentrations were around 200-500 mg/l. Experiments to determine the pH dependency,

which were carried out using this aeration System, indicated that a reduction to pH 10 had hardly any influence on the reaction speed.

However, problems arose during the experiments with blocked jets. The pH is effected by using carbon dioxide and the jets of the agitator tended to become blocked by the formation of calcium carbonate.

Therefore, diaphragm plate aerators were installed which were less susceptible to failure. Table 1 shows the results recorded for sulphide oxidation with differing aeration processes.

For the treatment of effluents containing chrome, precipitation of the chrome by hydroxide was considered. This process is used for the chrome recycling of residual chrome tanning floats.

However, it is also well known that chrome precipitation in the effluent stream brings about major problems for the wet finishing process. In lab experiments, therefore, chrome precipitation was investigated in the chrome containing residue floats produced during the post tanning processes in the manufacture of shoe upper leather, table 2.

Precipitation was carried out using mag-nesium oxide at pH 8.6-9.1. Chrome contents, before and after precipitation, and the COD value of the untreated floats were determined in order to quantify any dependency between the two.

Table 3:

Table 3 Investigations on optimal conditions for Cr-precipitation in the effluent of the post-tanning process			
Addition		Supernatant	
Ca(OH) ₃ up to pH	FeCl ₃ [ml/l]	pH	Cr, total [mg/l]
pH 12	1	11.4	1.0
	2	10.6	1.1
	4	9.6	1.2
	8	8.2	1.0
pH 11	1	9.8	10.3
	2	9.4	4.0
	4	8.5	1.4
	8	5.9	n.b.
pH 10	1	9.6	26.4
	2	9.2	11.0
	4	8.2	1.6

**The influence of
iron (III) was
investigated (3) and
slaked lime and iron
(III) salts (4)**

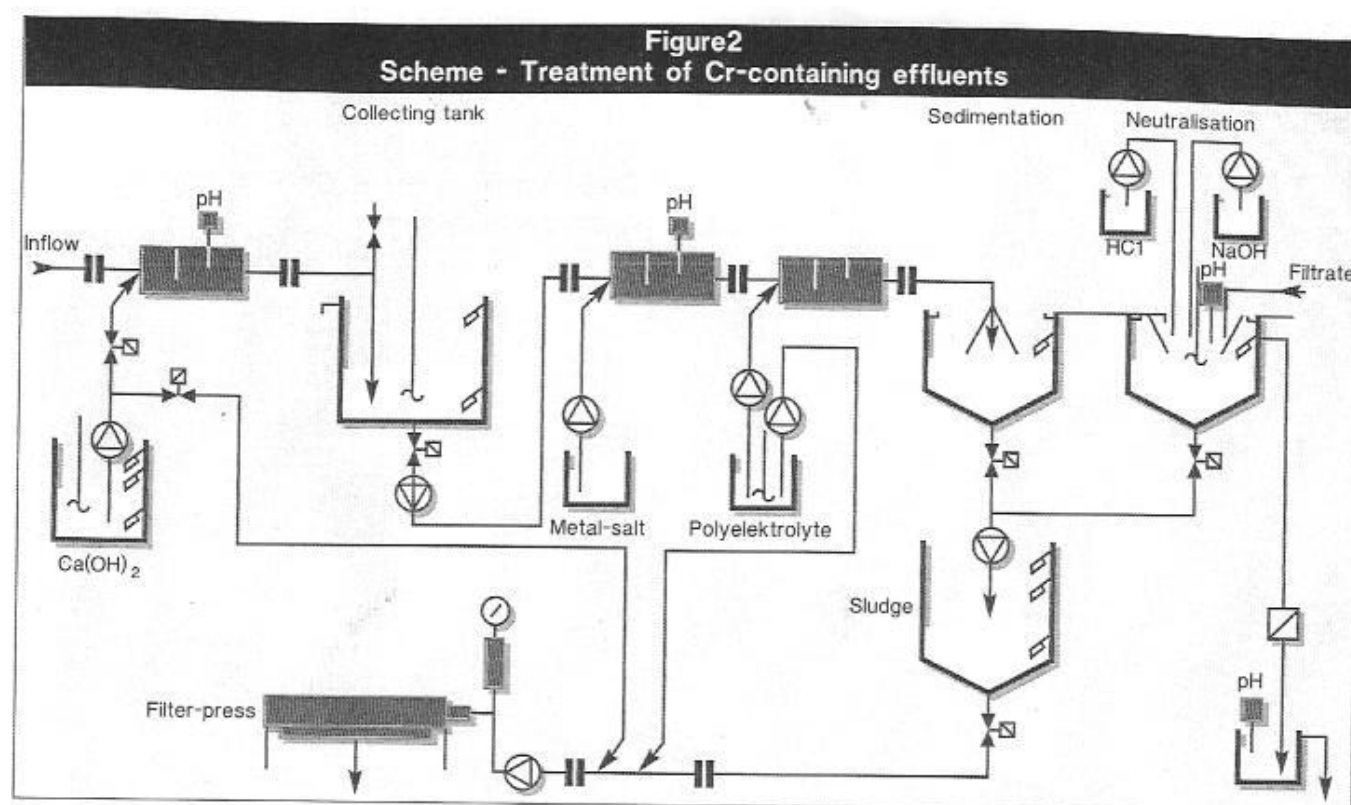
Table 4:

Table 4 Precipitability of Cr • dependence on pH and FeCl₃ - addition						
Effluent of post-tanning process COD 6440 mg/l • pH 3.8 • fat 1264 mg/l • Cr 58.8 mg/l						
	Addition		Supernatant		Sludge	
	Ca(OH) ₂ w = 0.05 [ml/l]	FeCl ₃ w = 0.13 [ml/l]	pH	Cr, total [mg/l]	Volume after 2h [ml/l]	d.s. [g/l]
pH 12	43.5	2	10.6	11	250	2.46
	43.5	8	8.9	10	250	2.48
pH 11	35.0	2	9.5	18	170	2.46
	34.8	4	9.3	10	160	2.32
pH 10	26.8	2	9.3	9.9	90	1.75
	27.4	4	7.9	18	110	2.00
w = mass portion d.s. = dry substance						

Investigations indicated that it was not possible to attain chrome values of below 1 mg/l using precipitation with magnesium oxide only. However, by additional filtration, using a fluted filter, a marked reduction of the chrome content was achieved except in the residual floats from fatliquoring and retanning. A dependency between chrome precipitation and COD was shown to exist. The floats with increased COD values produced a less favourable precipitation result, which could not be appreciably improved even with supplementary filtration. This suggests that under the influence of fatliquors and syntans, the chrome is clearly held as small particles in a solution or is at least stabilised in the float. These substances contain sulpho groups which can interact with the chrome complexes. If so, it should be possible to achieve an improved precipitation by increasing the pH. Experiments were carried out to test the pH dependency of the precipitation process. The pH value was set using lime milk. At the same time the influence of iron (III) Chloride was investigated, as the addition of ferne salts had proven successful in practice as an aid to precipitation. Table 3 shows the results for effluent resulting from the post tanning liquors of upholstery leather. The liquor samples were pH adjusted and after agitation for two hours the iron (DI) solution and 10 mg/l of polyelectrolyte were added. After a settling period of two hours, the chrome content in the supernatant liquor was measured. The results clearly show that increasing the initial pH value leads to a marked reduction of chrome in the liquid. In the case of the lower pH values marked improvements were also achieved by increasing the amounts of iron (EI) salts. At pH 12 this had no influence. As the objective of the study was sludge minimisation, the influence of slaked lime and iron (III) salts on it was investigated using a comparable effluent. The results of this test, table 4, indicate that the sludge volume measured after settling for two hours increases markedly with the increase in slaked lime. At the same time there was an increase of the solid residue but the quantity of ferric salt added had no effect. Scale up trials in a pilot plant, figure 2, were carried out to determine if the laboratory results could be repeated in practice. The chrome containing effluent was fed into a six m³ collecting tank, where slaked lime was added. A control device is used to regulate pumping of the effluent into the settling tank, during which the precipitation agents were added. The overflow from this tank is transported to the post neutralisation tank where the pH value can be set for discharge into the public sewage System. The precipitated chrome sludge is transported to a collecting tank from which the filter press can be fed if required. During the period of investigation the effluent to be treated contained 20 to 210 mg/l chrome. In order to set a pH of 9.5 in the collecting tank, between 670 and 2730 g Ca(OH)₂/m effluent were required. The pH in the collecting tank and the ferne salt additions were varied to determine the effect on the sludge volumes. It was not possible to obtain a pressable sludge in every case, which suggests an additional filtration aid would have to be used. This in turn would lead to an increase of the sludge quantity and increase the related costs. In table 5, results from these investigations are summarised. They clearly indicate the fluctuations caused by the post tanning process which affect the effluent and the chrome precipitation. Increasing the pH value in the collecting tank from 9,5 to

12.0 does not bring about any improvement for this liquor, from shoe upper production, in contrast to the experiments carried out with corresponding floats from the upholstery leather production process. There is a tendency for the precipitation to improve with greater use of reagents, but at the same time the incidence of sludge and the salt content is markedly increased. In one case, for example a 2.5 fold ferric salt addition led to a reduction of chrome content from 1.4 to below 0.5 mg/l but the sludge quantity increased by around 25%. In the search to minimise the incidence of sludge, the use of basic aluminates as a precipitation agent proved promising during laboratory testing, table 6.

Figure 2:



Compared with precipitation using ferric ions or an acid aluminium salt, the use of an aluminate, whose pH value permits operation without the addition of slaked lime, results in the reduction of the occurring dry sludge matter by a third. This substantial advantage is retained even in comparison with cases where calcium hydroxide alone is used and it produced a chrome content of less than 1 mg/l. When applying the laboratory findings to the pilot plant with a compartment type filter press, it still remains to be seen whether the comparatively bulky sludge can be compressed. Until the combustion of chrome containing sludges has been fully investigated landfill sites remain the most important method of disposal. The requirement of a solids content of at least 35% can be achieved by adding filtration aids or subsequent sludge drying. But, there is now a question of elution.

Table 5 and Table 6:

Table 5
Cr-Precipitation in the post-tanning effluent of upper-leather production

pH (collect tank)	Ca(OH) ₂ [mg/l]	pH outflow	FeCl ₃ [mg Fe/l]	Poly-electrolyte [mg/l]	Cr inflow [mg/l]	Cr outflow [mg/l]	Filter-cake [kg/m ³]	d.s. [kg/m ³]
12.1	865	6.4	472	4	52	<0.5	6.7 (28.0% d.s.)	1.9
11.8	850	8.5	208	11	74	1.4	6.7 (22.5% d.s.)	1.5
12.0	4000	11.6	93	15	125	2.1	7.0 (33.4% d.s.)	2.3
9.5	677	7.1	35	10	70	1.7	6.5 (21.0% d.s.)	1.4
9.6	729	7.1	144	12	39	0.7	5.6 (27.0% d.s.)	1.5

d.s. = dry substance

Table 6
Sludge amount produced in dependence on the precipitants

Effluent from post-tanning processes of upper-leather COD 2470 mg/l • Cr 25.7 mg/l							
Addition of precipitants				Supernatant		Sludge	
1. Ca(OH) ₂ [mg/l]	pH	2. product	[mg/l]	pH	Cr. total [mg/l]	Volume [ml/l]	d.s. [g/l]
511	11.0	FeCl ₃	98 (Fe)	8.2	0.4	150	1.5
511	11.0	"Al ³⁺ -"	126 (Al)	7.1	0.7	240	1.7
-	-	"[AlO ₂]-"	76 (Al)	9.1	0.9	220	1.0
511	11.0	-	-	-	0.9	160	1.4

d.s. = dry substance

In the German federal State of Baden-Württemberg, one of the main centres of the German leather industry, a recent ruling stated that the joint deposit of effluent purification sludge from tanneries with household refuse is now generally subject to eluate criteria. This ruling specifies maximum values of 1.5 mg/l AOX, 1.0 mg/l total chrome and 0.1 mg/l chrome (VI) in the eluate.

The filter cake produced in the pilot plant complies with the limiting values for AOX and chrome (VI). However, the total chrome content in the eluate is subject to fluctuations between 0.6 and 2.0 mg/l. Ageing seems to play a part in this fluctuation and further work is being carried out.

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