CHROMIUM RECOVERY THROUGH PRECIPITATION AND SEPARATION

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<th>Process step</th>
<th>Tanyard</th>
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<td>Description</td>
<td>Separation of chromium salts from the aqueous effluent stream by precipitation, with dewatering of the precipitate. Re-solution of the precipitated chromium using sulphuric acid, for use as a partial substitute for fresh chromium salts; or use of the chromium sludge as a raw material by another industry.</td>
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### Technical description

The technique is used for the treatment of effluents from the chromium-tanning process including washing floats and liquid from samming. It is based on the recovery of chromium from the effluents and its recycling into the production process. From the chemical point of view, chromium(III) recovery is a simple process with excellent environmental results, but it needs careful analytical control and it requires special equipment such as:

- A separate tank for collecting spent chrome tanning liquors.
- Material to analyse the chromium content, acidity, and alkalinity.
- A tank with stirrer and pH control for adding the right amount of alkali for the precipitation.
- A sedimentation tank for chromium hydroxide settling.
- A filter press or centrifuge for the chromium hydroxide sludge.
- A tank with stirrer and heating equipment for the re-solution of the chromium hydroxide by concentrated sulphuric acid.

When a double precipitation is needed, using fossil flour to absorb fats and other chemicals present in the spent chromium tanning liquors, more filter presses, more chemicals, more time, and higher costs are involved.

Chromium(III) can be recovered from the exhaust liquors (tanning liquors, samming water) from the conventional chrome-tanning process.

Chromium from high-exhaustion chromium salts is not recycled due to the low concentration. The liquors containing chromium are collected in a collection tank, after which the chromium is precipitated by addition of an alkali.

The precipitated chromium is separated from the supernatant, after which the chromium sludge is dissolved in concentrated sulphuric acid (for 1 kg Cr₂O₃ as precipitate about 1.9 kg H₂SO₄ is required). The supernatant is generally discharged to the effluent. The precipitate should be redissolved as soon as possible, as it gets less soluble with time.

Any alkali will precipitate chromium, but the stronger the alkali, the faster the rate of coagulation. One of the precipitation options given below can be
Sodium hydroxide or sodium carbonate (as strong alkali) will lead to a fast precipitation and voluminous sludge.

Fast precipitation with additional agents like polyelectrolytes to facilitate coagulation has the advantage that only simple dewatering is necessary.

Slow precipitation, e.g. magnesium oxide (as a powder, pH 8), gives a denser sludge, which allows for decanting. For 1.0 kg Cr$_2$O$_3$ in the spent liquors, 0.25 – 0.4 kg MgO, is needed depending on the basicity and masking.

Another advantage of the use of MgO is that any excess addition will not cause the pH to rise beyond 10, so that any sludge redissolving at higher pH levels is avoided. Impurities and process chemicals may build up and therefore an increased level of process control is needed, and impurities may need to be destroyed after dissolving the chromium sludge.

Achieved environmental benefits

Efficiencies of 95 – 98 %, 99 % and 99.9 % of chromium precipitation are reported. In the Netherlands, reported values, measured as total chromium in a daily composite sample, after sedimentation or flotation of the separate chromium-containing effluent before mixing, are 1 – 2 mg Cr/l.

The same levels are achieved in some German tanneries. A tannery in Sweden normally achieves chromium concentrations of <1 mg/l in the separated effluent containing chromium after precipitation. The discharge to the treatment plant after this internal measure is about 0.4 kg chromium per tonne raw hide.

Most of the chromium in the discharge to the waste water comes from the post-tanning operations (retanning, dyeing and fatliquoring) and these effluents are not passed through the chromium recovery unit.

Data from tanneries in the UK show chromium contents of 3000 – 6000 mg/l in the chromium liquors after tanning. Chromium precipitation can remove around 99.9 % of this chromium, which results in a concentration of chromium in the separated effluent of 3 – 5 mg/l and a concentration in the total effluent following mixing with beamhouse effluent of less than 1 mg/l. The recovered chromium sulphate solution can be recycled into the tanning process by replacing up to 35 % of the 'fresh' added chrome tanning salt.

As the overall chromium utilisation ratio increases, the amount of chromium discharged to the waste water is reduced. This results in a reduction of chromium in sewage sludge and chromium discharged to the environment. No additional waste volume is built up. In the Table the technique is compared to other methods of processing.

Environmental performance and operational data

Italy and Portugal each have one common chromium recycling unit. The plant in Italy was designed to receive 400 – 500 m$^3$ exhausted floats per day from about 250 operators. From this input the recovery plant produces 2 000 kg Cr2O3 per day, which is reused in the tanneries.

The tanneries mostly use a mixture of recycled and new chromium; 1 part recycled to 2 parts fresh chromium salts.

The primary driver for establishing this plant was economics, because energy is saved, since neutralisation and filtration take place without the need for heat, and because chromium is recovered and reused in the
Tanneries belonging to the co-operative, so there is less need to produce chromium by roasting chromite.

The second reason is the environmental benefit, because chromium is removed from the sludge discharged by the centralised purification plant.

One tannery uses the following recycling process. The effluent containing chromium must be collected as concentrated as possible. Magnesium oxide is added and the pH is brought to 8.5 – 9. After mixing for a couple of hours and adding a polyelectrolyte, insoluble chromium hydroxide and magnesium sulphate will settle. The supernatant has a chromium concentration of about 1 – 10 mg Cr/l and has to be treated with lime milk and iron(III)chloride before it can be discharged into the sewer. The remaining sludge is dissolved with sulphuric acid, forming chromium sulphate and magnesium sulphate.

After 24 hours of mixing the pH will be about 2, preventing the dissolving of magnesium sulphate. The recovered chromium sulphate has a chromium oxide content of about 20 gram Cr2O3/l and can be used in the tanning process for any type of leather when not more than 20 % is added, calculated on the active oxide.

There are certain types of leathers (e.g. the split) that can be tanned with 100 % regenerated chromium.

### Cross media effects

Chromium recovery requires the use of alkali, acids and auxiliaries. Consequently, the quantity of neutral salts discharged to the effluents is increased.

### Technical considerations relevant to applicability

Chromium recycling may result in a slight change in the colour of the wet blue and organic compounds can produce a greyish tint. The disadvantages are not as severe as in recycling the liquors, because a moderate concentration of organic compounds (fat, masking or high fixation auxiliaries, vegetable or synthetic tannins, small amounts of biocide) does not disturb precipitation and re-dissolving.

Chromium recovered in this way resembles more closely the quality of fresh chromium, and therefore this system of chromium precipitation tends to be favoured over direct chromium recycling. If the achieved quality of the final product is negatively affected by the use of recovered chromium, the chromium can be used for tanning of split, where there is a market for tanned splits.

The technique can be applied to both new and existing plants. It is independent of any local conditions and can be introduced in any tannery using chromium as a tanning agent. In practice, it has been applied in larger tanneries or in common effluent treatment plants. It is not appropriate for treating effluents from high-exhaustion chromium tanning. Leathers produced using recycled chromium can be used for automotive upholstery, but are not necessarily suitable for other applications.

### Economics

Slow precipitation has the advantage that no investment in filtering equipment has to be made. However, slow precipitation may not always be technically possible, as fat and protein impurities may interfere with the settling of the precipitated chromium.

Economic feasibility will depend on the exhaustion rate of the chrome tannage and the quantity of chromium liquors generated. In general, the...
lower the exhaustion rate during tanning and the higher the volume of the floats, the higher the economic feasibility.

The introduction of chromium recovery through precipitation and separation requires a substantial investment. Data from 2004 indicate that the investment cost for a chromium treatment plant for the treatment of 100 m³ water containing chromium will be approximately EUR 350 000 – 450 000.

### Driving force for implementation

The main driving forces are to reduce the chromium discharge from the tanning process and to reduce chromium consumption, and in one case regional legislation.

### Example plants

Several central chromium recovery installations have been constructed in European tannery conglomerations in order to benefit from economies of scale, e.g. Consorzio Recupero Cromo SpA, in Italy.

Some individual tanneries have also been able to implement chromium recovery on site, e.g. in Germany (e.g. Bader and Gmelich), Italy and Sweden (Elmo Sweden AB).

### Reference literature

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### Source

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### Key words

Chromium, industrial efluents; process water; reuse of materials