

Low Temperature Conversion of Cr-containing tannery wastes and sludges

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An extensive study was initiated at LGR in 1998 to investigate the thermal conversion of chrome leather wastes and sludges aiming at an avoidance of any Cr(VI) formation^[Legend 1]. The outcome from this detailed study shows that thermal treatment can reduce the volume of solids for deposit by a factor of approximately four and that formation of Cr(VI) can be avoided. In addition, a considerable amount of energy is made available in the form of a diesel-type fuel that may be used within the conversion process.

Leather production is inevitably linked to the creation of waste water and considerable amounts of by-products and solid wastes including the sludges from effluent treatment. Due to the increasingly stringent requirements governing tannery effluents regarding their chrome content, and due to problems involved in the disposal or utilisation of by-products containing chrome, chrome tannage in particular has come in for criticism.

Practically, tanneries have no alternative at present but to dispose of treatment sludge by landfill, and up to now leather waste is frequently deposited above ground.

However, with the German Landfill Decree regulations becoming applicable (as part of the implementation of the EU landfill directive) from June 2005, this form of disposal will no longer be permissible—without an appropriate authorisation by way of exception—due to the high organic component. Landfill of any material with more than 5% volatile solids ('loss on ignition') will be banned.

Initially, the most promising way forward would appear to be combustion, the primary benefit being a drastic reduction of the waste volume and mass, as well as meeting the limit set on volatile solids. According to research by Prof. Schwedt of the Technical University of Clausthal, Germany, it is possible to avoid emission of chromium (VI) into the atmosphere using this method for leather waste or chrome-containing sludge. On



Drying unit of the LTC plant

the other hand, the combustion ash will contain at least small portions of chromium (VI)—depending on the combustion temperature and holding time—and therefore requiring specialised handling and treatment.

The low temperature conversion technique

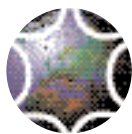
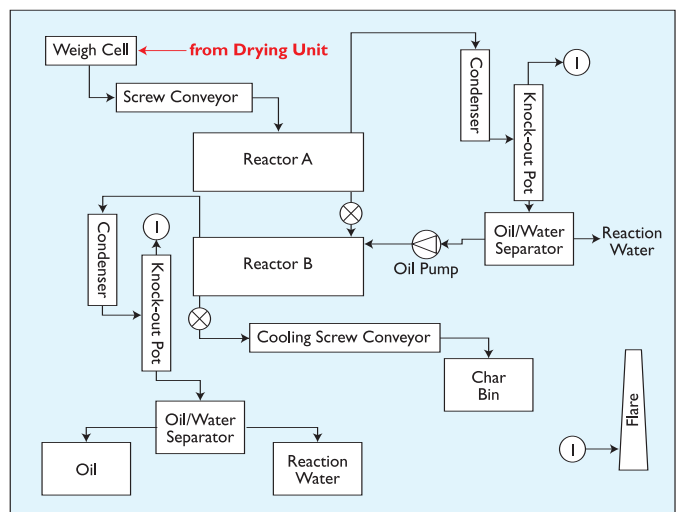
Studies were conducted to determine if chrome-containing sludges and shavings from the leather industry could be managed to meet pending disposal/reuse legislation. The technology chosen for these investigations was Low Temperature Conversion (LTC). This technique originated in Germany 20 years ago with Prof. Dr. Ernst Bayer, University of Tuebingen.

In essence, at about 400°C atmospheric pressure, and in the absence of oxygen, the solids are converted by LTC into four products:

- A char (or bio-coal)
- Bio-oil
- Non-condensed gases
- Reaction water

The process was developed mainly for the treatment of sewage sludge, offering the following benefits:

- High energy efficiency: recovery of energy in the form of conversion products that can be used as fuels ►

**Figure 1: LTC Plant - Conversion Unit**

- Volume reduction of the original residues that require disposal.
- Control of heavy metals: these are withheld from the environment as they are transformed into insoluble sulphides and retained in the char for potential recovery.
- Destruction of chloro-organic compounds such as PCBs, PCPs and dioxins.

In operation the dehydrated tannery sludge is fed directly into a fluid bed dryer to form dry granules. These are stored in a product silo, then extracted as feed for the conversion process.

The conversion process takes place in a two-stage reactor; a schematic of the LTC conversion unit is shown as *Figure 1*.

The dry granulated sludge is heated in the first reactor (*A*) to 400-450°C, and, in the case of sewage sludge, about 40% is converted to a gaseous phase. These reaction gases feed to the second reactor (*B*), using heated and insulated pipelines to avoid any condensation. The solid residue as char from the first reactor (*A*) is also fed to the second reactor (*B*) by means of a star wheel feeder.

In the second reactor (*B*), the reaction gases contact the char at 400-450°C. This enables catalytic gaseous phase reactions such as desulphurisation and decarboxylation, and the elimination of chloro and nitrogenous components.

Gaseous by-products from this conversion exit the reactor, and are then cooled to 30°C to form a mixture of condensed bio-oil and reaction water. The bio-oil is refined from the mixture using a separator, and this can be used as fuel within the fluidised bed-drying unit.

The pilot conversion plant

The pilot conversion plant^[Legend 2] used for these investigations provided a capacity equivalent to 20 kg of dry sludge per hour, and was fitted with a fluid bed sludge dryer. This was commissioned at the Sudleder Tannery in Rehau/Germany in May 2000.

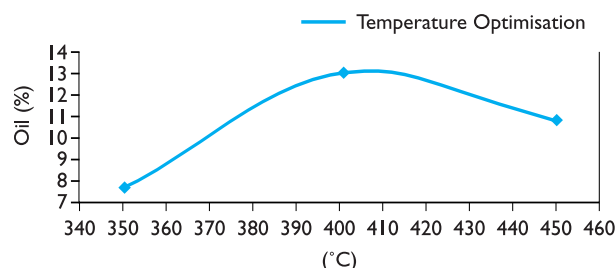
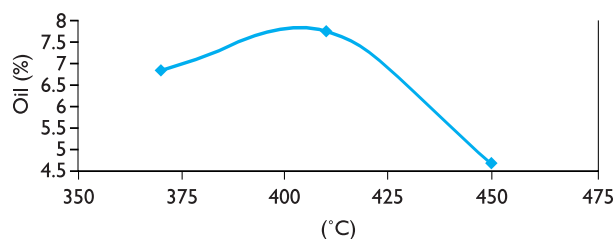
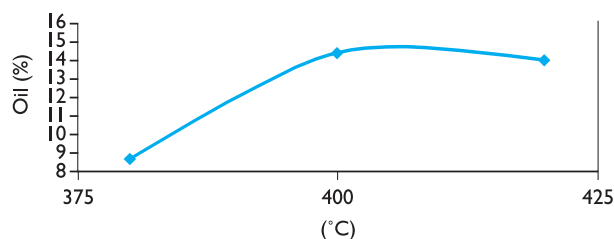
The programme involved the processing of sludges from three tannery wastewater treatment plants in Germany, a Brazilian tannery, and the processing of sludge/chrome shavings mixtures. In total seven different wastewater treatment sludges and sludge/shavings mixtures were processed as detailed:

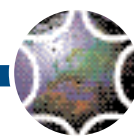
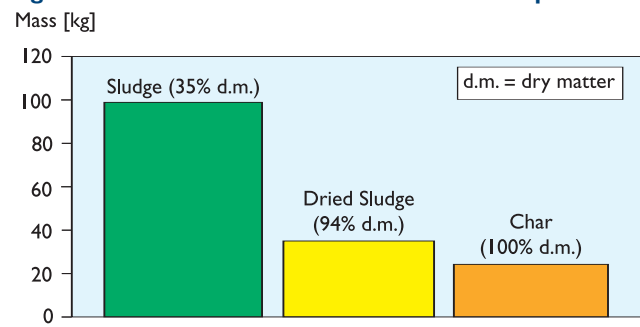
- two physical/chemical sludges from total effluent treatment, conditioned with lime and ferric chloride
- one sludge where polymer was used to condition the sludge for dewatering
- three biological sludges—two with chrome and one without
- a physical/chemical sludge from post-tanning
- a mixture of shavings and polymer conditioned sludge
- a mixture of three sludges with shavings from one tannery.

The conversion programme was based on a two-stage approach:

First: The optimal temperature for conversion was established. This was reached by converting the sludge at three different temperatures, with the maximum oil yield used as the indicator for the optimal conversion temperature.

Second: A set of trials was conducted at the optimal conversion temperature to generate data for mass, elemental and energy balances. This data was then used to assess the suitability of the technology for management of residues from the leather industry.

Figure 2a: Sludge – Phys./Chem. Treatment of Total Effluent**Figure 2b: Sludge – Biological Treatment of Cr-cont. Effluent****Figure 2c: Sludge – Biological Treatment of Cr-cont. Effluent from Post-Tanning**


Figure 3: Mass-Reduction of Solid Waste for Disposal


THE OPTIMUM TEMPERATURE

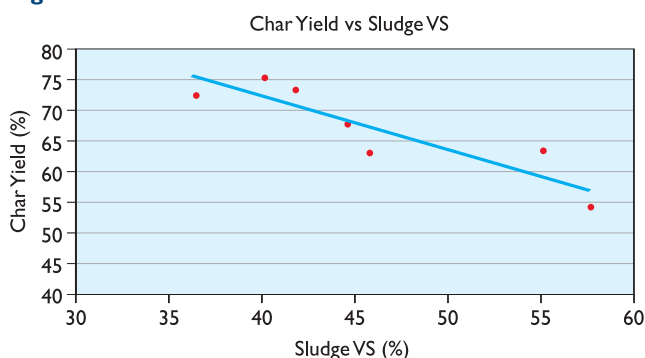
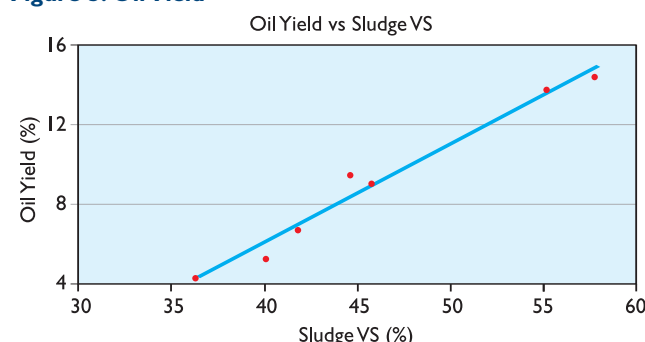
The optimal temperature to maximise oil yield was in the range of 400-410°C for all sludges tested. This is shown in Figures 2a,b,c.

The LTC process demonstrated that the quantity of residues (sludge and shavings) requiring disposal from tanneries can be reduced very significantly. Typically, the char requiring disposal is only 25% of the mass of the wet sludge cake and shavings disposed to landfill based on a typical dry matter content of 35% as shown in Figure 3.

Within the optimal temperature range, the char yields ranged from 55-75% and the oil yields from 5-15% as shown in Figures 4 & 5 respectively.

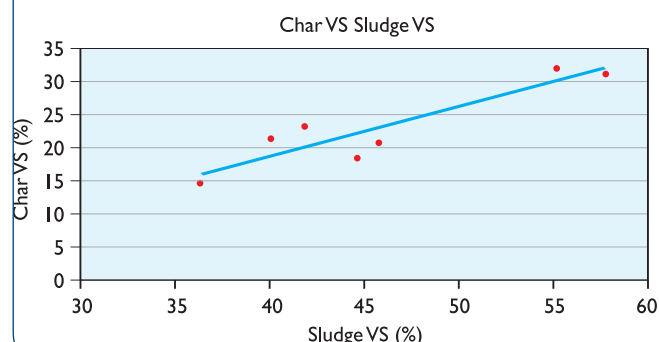
Both yields are strongly dependent on the volatile solids (VS) content of the feedstock. As the feedstock VS value rises the char yield decreases and oil yield increases.

The addition of shavings to sludge results in an increase in oil yield and a reduction of the char. However, for technical reasons associated with this pilot plant, the portion of shavings in the feedstock was limited to 20%.

Figure 4: Char Yield

Figure 5: Oil Yield

Figure 6: Heavy Metal in Bio-Coal and Leachability

(Heavy) Metal	Bio-Coal Metal Recovery [%]	(Heavy) Metal Leachability [mg/l]	German Landfill Directive (TASi) Class I [mg/l]
Aluminium (Al)	99.993	NR ²	
Arsenic (As)	NA ¹	< DL ³	< 0.2
Cadmium (Cd)	99.93	0.0005	< 0.05
Cobalt (Co)	100	NR	
Chromium (Cr)	99.99	0.03	
Cr (VI)	NA	< DL ³	< 0.05
Copper (Cu)	99.973	0.004	< 1
Iron (Fe)	99.997	NR	
Manganese (Mn)	99.975	NR	
Mercury (Hg)	NA	< DL ³	< 0.005
Nickel (Ni)	99.954	0.01	< 0.2
Lead (Pb)	100	0.008	< 0.2
Antimony (Sb)	100	NR	
Tin (Sn)	100	NR	
Zinc (Zn)	99.889	0.02	< 2

¹NA: Not Applicable ²NR: Not Regulated ³DL: Detection Limit

Figure 7: Volatile Solids Content of Char


THE PROPERTIES OF THE CHAR

The study clearly shows that essentially all of the heavy metals in the feedstocks are retained in the char product. Very importantly, no carcinogenic hexavalent chromium is produced in the conversion process as shown in Figure 6.

All chars produced met the German landfill decree requirements for the leachability of heavy metals with one exception, notably the char VS content as shown in Figure 7.

The char VS content is very dependent on sludge VS content and operating temperature. To meet this component of the German landfill decree (loss on ignition limitation of 5%) the char would need to be processed at a higher temperature. Exploratory trials suggest a temperature of above 650°C will be required to meet this limitation as shown in Figure 8.

It must, however, be noted that the char VS is entirely composed of non-biodegradable fixed carbon. This will not decompose in a landfill, so an exemption from this particular requirement may be possible through negotiations with the appropriate regulators. ➤

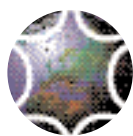
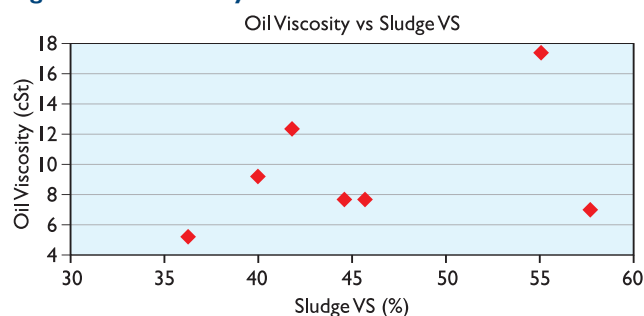


Figure 8: Bio-Coal Loss on Ignition (Volatile Solids-VS) as depending on Conversion Temperature

Trial Number	1	2	3	4
Temperature	550°C	550°C	600°C	650°C
Initial Bio-Coal VS	19.1%		25.0%	
Reaction Time	15 min		60 min	
Treated Bio-Coal VS	12.8%	11.2%	10.9%	7.4%
VS Reduction	33.0%	55.2%	56.4%	70.4%

Figure 9: Oil Viscosity



THE GENERATION AND PROPERTIES OF BIO-OIL

Conversion at approximately 400°C resulted in between 50-62% of the energy being captured in the oil, non-condensed gases and reaction water. Subsequent use in purpose-built combustors provides a significant proportion of the energy needed to dry the sludge.

All of the oils produced had high carbon contents, so the energy potential was high at approximately 40 MJ/kg. This energy density is more than 90% of diesel fuels.

The oil viscosity appears to be strongly related to sludge VS content, as shown in Figure 9.

The only oil that does not conform is that generated from the physical/chemical sludge from post-tanning. This is a very different sludge compared with the others, with a high VS (58%), but providing an oil with a relatively low viscosity of 7 mPa.s.

Experience indicates that oils with a viscosity of greater than 10 mPa.s (cSt) could only be combusted in the dryer burner if they were blended with diesel. In a commercial scale plant the burner would be designed to burn a combination of oil and non-condensed gases to maximise the energy content.

ABSENCE OF DIOXINS AND FURANES

Both the char and bio-oil were analysed for polychlorinated dibenzo-dioxines and furanes. Neither dioxines nor furanes could be detected in the bio-coal and the extremely low amount

Figure 10: Dioxine-Analysis of Conversion Products

	Bio-Coal	Oil	For comparison EU-Food limits (in fat)
Polychlorin. Dibenzo-dioxines and furanes [ng/kg]*	not detectable	0.09	3 (Beef) 1 (Pork) 0.75 (Veg. Oil)
* in WHO-PCDD/F - TEQ (= Toxicity Equivalents)			

Panel I

The behaviour of chrome within landfill

Studies on the landfill behaviour of chrome-containing sedimentation sludge performed by LGR and also by Prof. Dr. Schwedt of the Technical University of Clausthal, show that under normal controlled conditions no risks are posed to the environment.

The solubility of chrome around the neutral pH zone under these conditions is extremely low (i.e. only a few per cent), and drops still lower with time. As a result of ageing the chromium hydroxide slowly transforms to the completely insoluble oxide stage. In addition, under these conditions only the non-hazardous chrome(III) compounds exist.

of 0.09 ng/kg detected in the oil is still far below the EU food limits of 0.75-3 ng/kg fat. Comparisons with edible oils is shown in Figure 10.

THE REACTION WATER

The reaction water shows a COD of 93,000-120,000 mg/l and an NH₄-N value of approximately 32,000-50,000 mg/l at a pH of about 9.5.

Summary of findings

Comprehensive investigations into the low temperature conversion of sludges and chromium-containing shavings showed that the volume requiring disposal can be reduced by at least a factor of four. In addition, these materials can be successfully converted into industrial fuels as bio-oil and non-condensed gases, and as a char or bio-coal for landfill.

A most important finding is that heavy metals—including chromium—are retained in the char. Critically, no toxic hexavalent chromium is produced in the process.

Char yields ranged from 55-75% and oil yields ranged from about 5-15% of the feed. The energy in the oil, non-condensed gas and reaction water can supply almost all of the energy needed to dry the sludge before conversion.

With the exception of the volatile solids (VS) content of the char (or loss on ignition), all other requirements for landfilling the material, as per the new German Landfill Decree regulations, are met. However, since the VS is entirely fixed as non leachable carbon, this parameter should be exempted for landfilling of the char.

Legend

1. This study is within the framework of the German-Brazilian co-operative research project on 'Pollution Prevention and Control in the Leather Industry'.
2. Environmental Solutions International (ESI), Australia, provided the pilot plant.

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