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22489

Project No. US/CPR/92/120 & UNIDO Contract No 98/186

Tannery Sludge Compost

Final Report

Northwest Institute of Light Industry, China

March, 2000

for

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

1 Introduction

In 1998, about 100 million standard pieces of leather were produced in China's tanneries accompanied by the production of about I million tons of tannery sludge (water content is 70%). The sludge was regarded as waste to be landfilled or piled on either municipal landfills or at the tannery itself. The high chrome contents and the malodour created growing environmental problems. Thus the identification of a sound way of disposal for the tannery sludge has been an extremely urgent task for the leather factories. The United Nations Project was established under this background and received a warm welcome and great attention from China Leather Industry Association.

The project was implemented under the leadership of China Leather Industry Association and UNIDO. Northwest Institute of Light Industry was appointed as responsible execution agency together with Xuzhou Globe Eagle Leather Group.

The aim of the Project was to identify possibilities for utilization of tannery sludge as fertilizer.

Within the programme „Safe disposal of tannery sludge", the North-West Light Institute for Light Industry Xian was contracted (no. 98/186) for the following tasks:

- execution of laboratory tests of sludge liming
- investigations of mobility and accumulation of chrome in soils and
- possibilities for composting of tannery sludge.

Composting of tannery sludge was foreseen to be carried out at Xian tannery. Due to the changed ownership, Xian tannery rejected to continue its cooperation with the UNIDO programme. Thus, the tests have been carried out at Xuzhou Globe Eagle tannery. Within the activities a complete rehabilitation of waste water separation and collection system including the improvement of chrome precipitation plant was introduced in order to separate chrome containing waste water completely from the other waster water streams.

2. Composting of tannery sludge

2.1 Introduction

The Tannery Sludge Program supported by UNIDO started in August 1998 and was jointly implemented by Northwest Institute of Light Industry and Xuzhou Globe Eagle Leather Group.

The target of the Project is to use tannery sludge for production of compost which can be further used as fertiliser or soil conditioner.

From the situation in Yue village (compare chapter 3) where sludge was used for more than 20 years as a fertilizer, it became clear that utilization of sludge presupposes the solving of the chrome problem.

Consequently one main aim of the project was to introduce sound solutions for separation, collection, and treatment of chrome containing waste water streams within the tannery and to improve the operation of the effluent treatment plants.

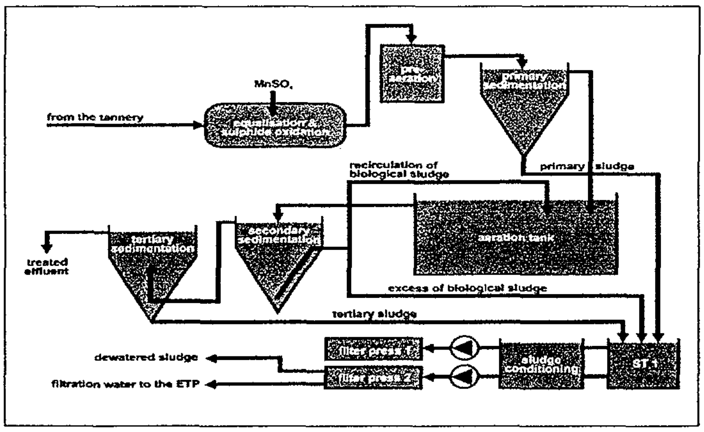
2.2 Xuzhou Globe Eagle Tannery Group

The Group Corporation is located in Xuzhou City situated at a major crossing of the east-west and north-south national railway lines about 600 km south-east of Beijing. The Corporation includes 4 tanneries of which three are using chrome as tanning agent. The production is about 2,500 cattle hides per day. Main products are shoe upper and garment leather.

In full production the factory produces about 3,000 m³ of waste water per day including 150 m³ of chrome containing waste water. The sludge production is about 33 m³ (at 30% ds) per day.

2.3 ETP

The effluent treatment system used consists of pre-treatment including mechanical sieving, sedimentation and mixing, aerated biological treatment system and second sedimentation and discharge.



The sludge received from the first and second sedimentation tank is naturally dried and disposed, the active sludge is dewatered by using a filter press after flocculation and sedimentation. After optimisation of the ETP the concentration of chrome in the effluent dropped well below the national standard.

2.3 Chrome collection and precipitation system

Chrome containing waste water is treated by using NaOH precipitation system. The chrome concentration after pre-treatment was still 16 – 66 mg/l indicating the low efficiency the system.

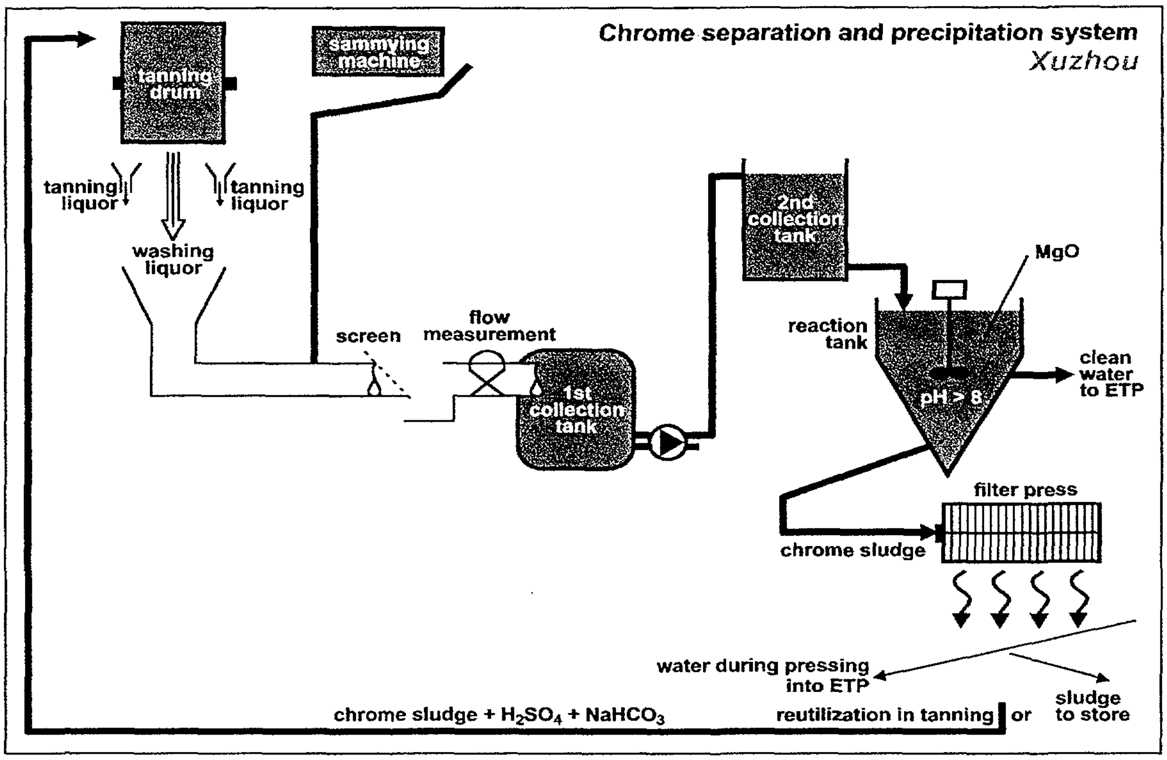
Main **problems** to be solved had been:

- The insufficient capacity of the chrome precipitation system does not allow to treat all waste water. Thus, about 40% of the sludge was drained directly in the ETP, with an resulting chrome concentration of about 10 mg/l in effluent and about 28 g/kg (ds) in the sludge.
- no functioning separation of waste water streams
- leakages in waste water channels
- mixing with rain due to broken covers of the channels
- no further dumping possibilities resulted in huge amounts of sludge stored at the factory side.

Consequently the project measures started with a complete rehabilitation and renovation of the chrome separation system including the chrome precipitation. Main **achievements** are:

- separation of chrome containing waste water by using automatic controlled gates
- quantitative collection of chrome containing waste water from all major sources
- electronic measurement of total and chrome containing waste water streams for monitoring, control and for fee purposes
- collection of chrome containing waste water in subsurface collection tanks with sufficient screening
- connection of all chrome sources (e.g. tanning drums, sammying machine,) to the system
- introduction of new precipitation technology using MgO instead of NaOH.
- installation of a second filter press in the precipitation plant
- erection of storage place for chrome containing sludge cake from the precipitation plant

After completion of collection and chrome precipitation system the chrome concentration in the ETP sludge dropped also down from about 20 ~ 30 grams to 1.5 grams per kilogram, which provides the basis the production of compost from tannery sludge.



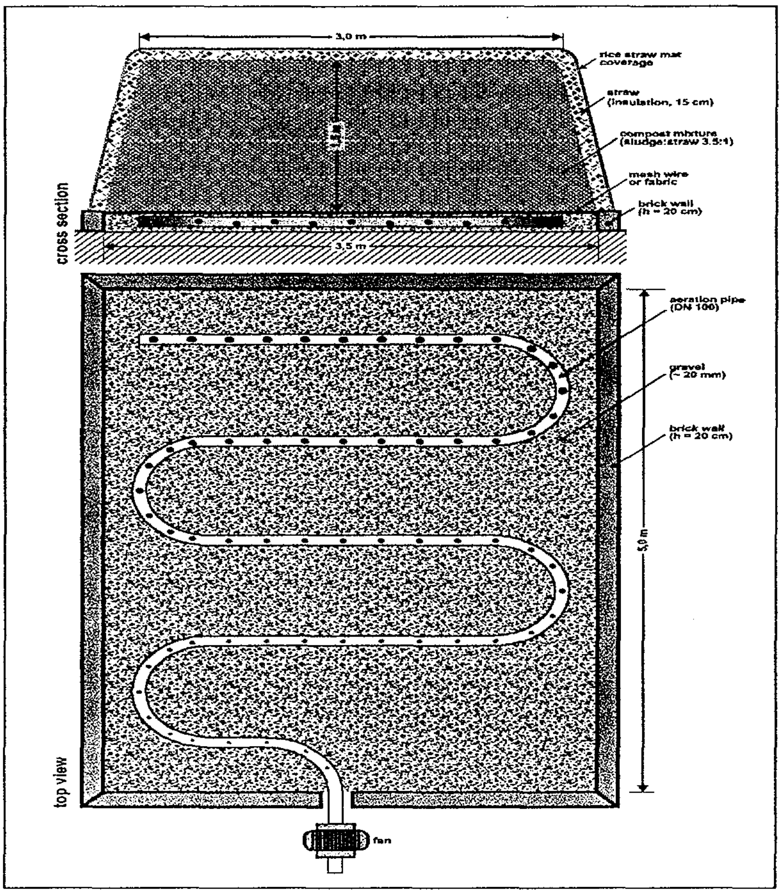
2.4 Composting

2.4.1 Site preparation

- The entire area was plastered cement/concrete and covered by a roof. On the floor a 20 cm high wall (using bricks or equivalent material) is build. After installation of an aeration pipe the space between the pipe was filled with gravel (grain size about 2cm). The aeration pipes are made of DN 100mm PVC material. Holes drilled in the pipe vary in diameter (8mm – 12mm) and distance (5cm – 10cm). Thus, approximately equal hydraulic conditions can be achieved throughout the hive. On the gravel a cover prevents entering of sludge into the gravel and pipes. The cover may be of fine mesh wire, rice mat or even used filter clothes from filterpress.

2.4.2 Construction of hives

Based on the design criteria and the basic characteristics of the compost raw material the dimension and composition of the compost hive have been calculated as being:



Windrow shape:	trapezoidal
Windrow cross-section:	4 m² at minimum
Windrow size chosen:	1.5m:3.5m:3m (height : base width : top width)
	cross-section: 4.9 m²
	length: 5 m
	Total volume: 22 m³.

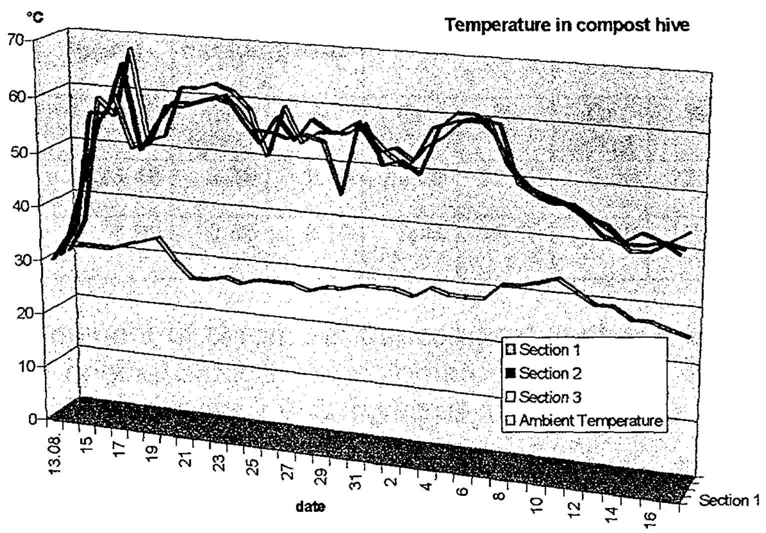
Finally 6 compost tests with different raw material and mixtures have been executed from between May to September 99:

- **May 19 to June 28:** two hives
  sludge : rice straw -3.5:1
  sludge : rice straw : vegetable leaves = 6 : 2 : 3.75
- **May 30 to August 6**
  sludge : rice straw = 3.5 ; l
- **August 12 to September 20**
  sludge : rice straw =3.5:1
  sludge : rice straw ⁼ 7 : 0.5
  sludge : vegetable leaves 1:1.

2.4.3 Process controll

The process is controlled by the following parameter:

- water content is 50% ~ 60%; moisture is controlled by changing ventilation. Sucking air through the hive (negative pressure) lowers evaporation losses, while blowing (positive pressure) increases evaporation losses.
- temperature at least 5 days above 55°C in order to destroy pathogen germs. The temperature is measured and controlled automatically.
- Water content is controlled twice a week. Optimal range is between 55% to 60%. If necessary, water is added.



2.4.4 Laboratory tests

The main contents of tannery sludge have been analyses prior to composting. For comparison the properties of municipal sludge from Xuzhou municipal ETP have been analyzed too. The results are compiled in Table 1.

Table 1: sludge composition		
item	**tannery sludge**	**municipal sludge**
water content (air dried) (%)	72,1	70,9
total solids (%)	29,7	29,1
volatile solids (%)	45,1	39,9
organic matter (%)	69,7	50,75
ash (%)	30,3	49,25
C (%)	18,90	20,88
N (%)	4,88	4,35
NH_4-N	0,14	
P_2O_5 (%)	6,36	0,17
Cr total (ppm)	1,500	21,76
pH	8,05	6,9

Except chrome both sludge samples are more or less similar. The amount of nitrogen in municipal sludge is surprisingly high and in the same range as the tannery sludge.

In a second analysis the chrome content of the tannery sludge has been determined according to plant availability and mobility. The samples were taken from the fist batch. At his time the chrome level was at the previous level, because chrome precipitation system was still under rehabilitation. The results are presented in Table 2:

Table 2: Chrome concentration in soils

sample	**total chrome (ppm)**	**water soluable+ exchangeable**		**elementary / adsorbed**		**organic incorporated**		**residual**		**summ**	
		Cr (g/kg)	%	Cr (g/kg)	%	Cr (g/kg)	%	Cr (g/kg)	%	Cr (g/kg)	%
sludge	28,48	0,39	1,36	23,06	81,89	3,50	12,42	1,22	4,32	28,10	100
compost 1	4,95	0,46	9,19	3,44	69,59	0,76	15,31	0,70	14,18	4,95	100

The development of chrome in the compost is shown in Table 3. From the first batch with original sludge, the chrome concentration dropped down well below the national standard of 1,000 mg/kg ds in compost no. 3.

Table 3: Development of chrome concentration (g/kg ds)

compost no	**date**	**Cr_{total}**
1	may 99	4,95
2	june 99	3,07
3	august 99	1,36
4	september 99	0,634

2.4.5 Tests on Farmland and in pots

First tests have been executed by using pots with wheat in the Institute itself.
A field test was carried out on a field nearby the factor in the suburb of Xuzhou City. An 200 m^2 of an rice field was marked and fertilised with compost. The area beside was chosen for comparison reasons. Main results achieved are:

- rice plants on the test field are in average 3 ~ 5 cm higher
- the yield per plant is 11 g higher which amounts to about 10%.

In addition some 30 pots of flowers were planted in the nursery of Xuzhou City. They were observed and have grown well.

2.4.6 Production regulations and monitoring

Production regulations and a monitoring system for composting were elaborated and introduced. The include:

- size of stalks and sludge particles
- temperature control (hourly)
- sampling procedure for measuring of total solids and water content (twice a week)
- daily recording of all data
- final test of compost.

The laboratory analyses include:

- total chrome,
- pH value,
- suspended solid
- sulfide
- ammonia nitrogen in sludge prior to composting and
- nitrogen,
- phosphorus
- potassium
- density
- total solids
- water content
- in finished compost.

2. Chrome accumulation in soils and crops

2.1 Introduction

Chrome containing tannery sludge is used since more than 20 years in Yue village (Changan County), which is located about 0.5 hrs from Xian city. The farmers do use sludge from the tannery since 1976. From 1976 until 1981 the whole sludge was used on all fields. Since the privatisation of the fields in 1981 sludge is used by those farmers who could organise transport.

This opportunity was used for the investigation of long-term accumulation of chrome in soils under practical conditions.

The area is slightly undulated with medium to heavy soils of neutral characteristic. Straw is used for melioration in order to improve porosity. Main products are wheat, rice vegetables and fruits.

The sludge is used as fertiliser for vegetables (cucumbers, tomatoes, water melons) and for wheat and rice production and is described by the farmers as long-term active with excellent fertiliser characteristics:

- Nutrients are released slowly over the whole growing period,
- remarkable higher production rates have been reported (up to 100%)
- the sugar content of water melons are remarkable higher than compared with water melons grown without sludge
- common root diseases of tomatoes and cucumbers which have to be treated by using $CuSO_4$ could not be detected in fields fertilised by sludge.

Sludge is stored along the fields and air dried. It is applicated either by distributing sludge on the fields prior to ploughing or direct to the plants after mixing with soil.

Due to the high chromium content of the tannery's sludge (even now, after installation of an direct recycling system the concentration of chrome is about 20 g/kg ds), the existing application method and soil monitoring is not acceptable and not in conformity with international and/or national standards.

2.2. Analysis of chrome in soils

A first brief survey was carried out in November 1998 covering the whole area of Yue village. Main target was to identify suitable methods for soil sampling and analysis.

For sampling the area was divided into three units with similar conditions in respect to topography and soil condition . From each of this areas one soil sample per 1,000 – 1,500 m² was taken from 0-20 cm depth (sampling date:

1998/11/12). All samples of one area were dried and well mixed. Beside, 5 crop samples were collected parallel at each location.

Table. 4: Description of samples

Sample no	Terrain, humus grade	Period of sludge manuring	Crops planted
1	sloped field, humus grade 2	non	wheat
2	sloped field, humus grade 3	non	wheat
3	top level of hill, humus grade 3	continuously, in 77-83; discontinuously, in 83-90; continuously, in 90-95.	wheat watermelon for few years.
4	top level of hill, humus grade 3	continuously, in 77-83; discontinuously, in 83--90; continuously, in 94-96.	wheat watermelon, for a few years
5	sloped field, humus grade 2	discontinuously, in 83 - 95	wheat
6	flat field, humus grade 1	continuously in 77-83; discontinuously, in 83-95.	wheat rice, in 77 - 83

Remarks: 1: No 1 is located 1Km away from Yue Cun village, it is considered as representative sample for unpolluted fields

First analyses were executed by using H_2SO_{4conc} for chrome extraction. The results showed low values which seemed not to be very reliable. Additional tests using $KClO_3$ and mixed acid ($HCLO_4$, HF, H_2SO_4) showed much higher values. The results are compiled in Table 5

Table 5: Chrome values by various analytical methods

sampling location	Cr Content (ppm)		
	$KClO_3$ Oxidation	Mixed Acid	H_2S0_4-H_20_2
l	18.25	62.46	7.901
2	26.75	81.48	14.31
3	123.03	189.47	48.26
4	88.94	157.36	33.92
5	25.97	100.00	23.31
6	38.02	128.56	25.92

The mobility of chrome in soils mainly depends on the adsorption characteristic of chrome.

Table 6: Adsorption stages and effects on mobility and crop availability			
stage	**mobility**	**crop availability**	**analysing method**
water soluable	very high	easy	H_2O
exchangeable	high	easy	1mol NH_4Ac
elementary / adsorbed	low	low	2mol HCl
organic incorporated	non	non	2mol HCL-5%H_2O_2
residual	non	non	$KClO_3$ under heat

The above mentioned methods have been used for determining the different chrome concentrations in this report. The results are compiled in Table 7.

Table 7: Chrome concentration in soils													
sample No	total chrome (ppm)	water soluable+ exchangeable		elementary / adsorbed		organic incorporated		residual		summ		Differenz in total chrome	
		Cr (ppm)	%	Cr (ppm)	%	Cr (ppm)	%	Cr (ppm)	%	Cr (ppm)	%	(ppm)	relative error
1	81,48	0,16	0,27	1,15	1,92	6,49	10,99	52,03	86,95	59,83	100	2,63	4,3
2	81,48	0,19	0,25	1,61	2,1	7,71	10,06	67,12	87,59	76,63	100	4,85	6,1
3	189,47	0,23	0,13	45,55	24,82	48,58	26,47	89,15	48,58	183,51	100	5,96	3,2
4	157,36	0,12	0,09	32,65	23,76	36,5	26,57	68,1	49,57	137,37	100	19,99	13,6
5	100,00	0,008	0,10	10,54	12,63	8,6	10,31	64,18	76,95	83,4	100	16,6	18,1
6	128,56	0,15	0,14	9,92	9,45	14,46	13,78	80,38	76,52	104,91	100	23,66	20,3

2.3 Analysis of chrome in crops

5 samples of wheat planted at the respective soil sampling location were taken per location, air dried and mixed. Grain, stems and roots have been analyzed separately for every sampling location by using diphenyle carabzide colorimetric method. The results are presented in Table 8.

Table 8: Chrome concentration in different parts of wheat plants

sampling location	chrome concentration (mg/kg)		
	grain	stem	roots
1	<0,1	0,13	0,20
2	0,48	2,73	5,58
3	12,23	17,08	22,04
4	11,53	12,22	13,91
5	1,47	2,43	4,48
6	5,27	5,91	8,01

2.4 Interpretation of results

2.4.1 Chrome in soils

The 6 samples can be clearly divided into three groups:

- **samples 1 and 2** originate from uncontaminated soils, thus reflecting the zero value or natural background. The values are within the common international range of 5 to 100 mg/kg ds chrome and within the values reported for the Shaanxi Plain (65 mg/kg ds). Thus, most of the chrome concentration in samples 1 and 2 are of residual character (about 85%).

- **The second group comprises samples 5 and 6:** On this soils sludge has been supplied for several years in the past, but application was stopped some years ago. This is reflected by the higher portion of mobile chrome.

- **The third group comprises the samples 4 and 5** which were taken from fields currently still manured by chrome containing sludge. The residual portions are comparable low, the easy soluable portions are comparable high.

In general most of the chrome in all samples derives from geological sources (rocks, minerals) and represents the natural background. Additional applied chrome is mainly adsorbed in mineral-organic complexes at locations were exchange with other Cations is easy. The results indicate that chrome adsorbed at or in organic-mineral complexes is again released and washed out or taken up by plants. Based on an average zero level of 72 ppm (mean value of sample 1 and 2) the total accumulated chrome can be assessed at being:

sampling location	non –residual chrome (ppm)	% of total
3	117	62
4	85	54
5	28	28
6	57	44

There are no quantitative figures about total chromium input during the years available. However, it can be assessed that the annual increase of chromium values is not exceeding 9 mg/kg*year (artificial added chrome in samples 3 and 4 dived by years of application).

2.4.2 Chrome in crops

The results of crop analyses show a clear coincidence between the chrome concentration in soil and chrome concentration in crops. Within the plant chrome concentration is highest in the roots (source of uptake), followed by stems and grain. The grain produced on the fields 3 and 4 exceeds the national standard of chrome in grain (<5mg/kg ds) by far.

3. Experiments of lime fertilizer produced from tannery sludge

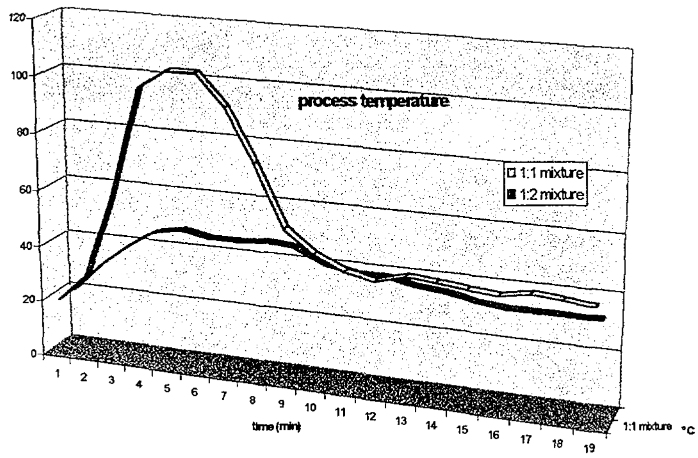
Lime fertilizer may be used as soil conditioner especially in acidic soils. Sludge might be used as raw material for lime fertilizer due to:

- the high contents of nutrients
- the stabilization of chrome in a basic environment
- the occurrence of both lime waste and sludge within the tannery
- the high process temperature destroys all pathogene germs eventually available in the sludge.

Sludge and active lime were mixed in two portions (1:1 and 1:2).

3.1 Results

As expected the temperature rose during the mixing and reaction process considerably up to more than 100°C. The final temperature depends on the portion of lime used.



The chemical analyses are compiled in Table 1. Water is evaporated during the reaction process. The final water content drops down from about 70% to 38% (2:1) respectively 13% (1:1). Considerable losses are to be reported for nitrogen due to conversion to NH^3. During the process some of Cr^{3+} was reduced to Cr^{6+}.

Table 9: chemical characteristics

sample	Organic matter (%)	C (%)	CaO (%)	pH	Total N (%)	P_2O_5 (%)	Total Cr (g/kg)	Cr^{6+} (ppm)	water content (%)
1:1	24,66	11,47	40,15	12,3	0,06	0,46	3,28	1,60	13,3
2:1	28,80	13,78	25,56	12,0	0,07	1,26	6,96	1,58	37,6

3.3 Conclusion

The sterilization of sludge by using active lime is not feasible for tannery sludge due to:

- the high losses in nitrogen reduced the values as fertilizer
- the creation of Cr^{6+} excludes any further utilization of food production or land application.