

Evaluation of Chromium Recovery Opportunities in a Leather Tannery

THOMAS C. VOICE, MACKENZIE L. DAVIS, GREGORY B. JOHNSON, and
LINDA L. STURGESS

*Department of Civil and Environmental Engineering
Michigan State University
East Lansing, MI 48824*

ABSTRACT

The opportunities for recovery of chromium(III) in cattlehide tanneries were investigated by reviewing the recent literature on chromium recovery techniques, performing an intensive sampling and analysis program in such a plant, and conducting a series of laboratory treatability studies. It was concluded that direct reuse of spent tanning liquors provided the most cost-effective means of recovering soluble chromium from this source. Recovery from solid waste streams, such as shavings and trimmings waste, is feasible using incineration. The cost-effectiveness of this approach will depend upon numerous external factors, however.

INTRODUCTION

Approximately 17 percent of the chromium consumed in the U.S. is used in the leather tanning industry [1]. Of this, 47 percent was fixed in leather products. The remainder was lost as shavings and trimmings waste and in the wastewater and wastewater sludges. The loss of chromium is of concern for three reasons:

1. the United States is totally dependent on imported chromite ore as a chromium source, and the stability of the major sources is questionable;
2. chromium that enters the tannery waste streams represents the loss of a valuable raw material; and
3. chromium in the tannery waste streams also represents an increasingly expensive waste treatment problem.

This paper reports the result of a study that was undertaken to evaluate the potential for chromium recovery in a leather tanning plant. While some of the findings are specific to the operations of the particular facility, most of the discussion is applicable to chromium tanning operations in general.

BACKGROUND

The technical feasibility of recovering chromium from tannery wastewater was demonstrated during World War II. The economics of the process were found to be unacceptable when the war was over, however [2]. In the intervening years, numerous attempts have been made to find technically and economically viable means for recovering the chromium. This literature survey is a summary of the research that has been conducted since 1950. The results of the survey are divided into two broad categories: process change and chromium recovery.

The feasibility of process change is strongly dependent on the effect the changes have on the product leather. They are presented here for completeness and because they have potential for significant savings. They are not considered in the experimental work reported here because they are beyond the scope of this study. The chromium recovery systems that are reviewed include: activated carbon adsorption; resin ion exchange; liquid ion exchange; precipitation/dissolution; and incineration.

Process Change

Harnley [3] first proposed direct recycle of chromium liquors by the replenishment method in 1951. In this process change, the spent liquor was adjusted to the original volume and refortified with chromium, salts and masking agents as required. Experiments conducted by Berund [4] and Thorstensen [5] in a paddle tanning system revealed that the number of cycles that could be carried out was limited because of the build-up of salts.

Miller [6], Davis and Scroggie [7-12], Covington [13] and Arnold and Covington [14], conducted studies of recycle with replenishment in drum tanning systems. Davis and Scroggie performed tests ranging from laboratory scale to full scale. In general they found that, using Baychrome A and Chromosal B in laboratory scale tests, they were able to recycle the chromium liquors 13 times over a three week period with no deleterious effect on the product leather. Sephadex gel chromatography was used to observe the differential uptake of the various chromium species (Figure 1). The results indicate that the chromium tanning liquors contain essentially the same molecular weight and charge distribution of complexes at the beginning and end of the first and thirteenth cycle. Three full-scale trials were run at three different tanneries. Seven, nine and eighteen cycles of reuse were examined. In each case the trials were terminated solely on the grounds of convenience. It was consistently found that sulphate salts built up in the first 3 to 4 cycles and then leveled off (Figure 2). This salt was shown to be removed during subsequent wet processing of the leather. The leather was examined by experienced tannery personnel for "feel," grain appearance, "break," veininess, Lastomer distention at grain crack, and burst. From run 3 on, the finished leather showed no consistent difference between the matched controls and those processed with recycled chromium. One of the major conclusions of Davis and Scroggie's work was that poor chromium exhaustion was not due to the presence of inactive complexes in the chromium liquor but was simply a mass-action effect.

In the 1980's Luck [15,16] developed a method to improve the mass transfer of chromium into the hide. The method depends on the use of a "self-basifying, organically masked, chromium-III sulfate tanning material" with the proprietary name Baychrome 2403. The quantity of unused chromium in a recycle/reconstitution system was compared to a non-recycle system using Baychrome 2403. The results indicate that the unused chromium in the recycle system was 2 to 3.5 kg of chromium oxide per 1,000 kg of hide. In comparison, a "good exhaustion" technique resulted in about 0.8 kg of chromium oxide per 1,000 kg of hide that was not being used.

Recovery

In 1959 Petrusche [17] concluded that ion exchange would be impractical because dilute acid solutions had to be used in the regeneration step to prevent a breakdown of the resin. Weber [18] calculated that recovery of chromium by

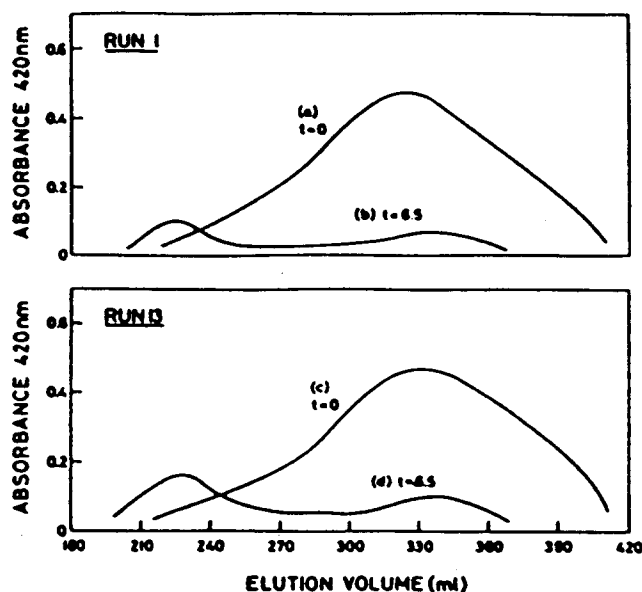


Figure 1. Sephadex gel filtration patterns of fresh (run 1) and recycled (run 13) chromium tanning liquors. Reprinted by permission from ref. 9.

ion exchange would be prohibitively expensive because of blockage of the exchange columns and high regeneration costs. Although not used routinely in the tanning industry, ion exchange has proven highly efficient in the electroplating industry [19]. Though Cr (VI) is more easily recovered than Cr (III), Cr (III) is routinely removed from process solutions [20]. Most modern exchange resins are resistant to chemical and thermal attack, but are subject to

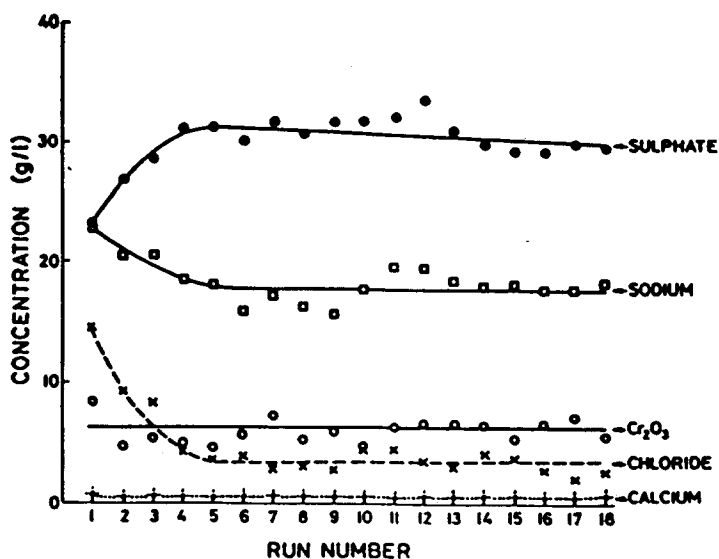


Figure 2. Concentrations of salts in the residual chromium liquors after tanning with recycled solutions. Reprinted by permission from ref. 11.

clogging and fouling. JRB Associates [19] suggested that improvements in filtration techniques, increased resin lives and better regeneration properties have evolved since the 1959 and 1973 reports and that ion exchange warrants renewed investigation by the tannery industry.

Early carbon adsorption studies by Petruschke [17] indicated that little if any chromium was removed from spent tanning liquor. Nelson [21] treated chromed leather with 5% oxalic acid and 10% ammonia and used this leather as an adsorbent for chromium solutions. Between 40 and 80 mg/L of chromium nitrate was removed from a test solution containing 200 mg/l of chromium nitrate. The contact time was 18 hours.

Precipitation followed by dissolution to recover chromium was first practiced during World War II. Since then, a number of individuals have reported experimental results [2,17,22,23]. Fields [22] conducted experiments using sodium bicarbonate, sodium carbonate, calcium hydroxide, magnesium oxide and sodium hydroxide in combination with a polymer. He found that sodium bicarbonate would not completely precipitate all of the chromium; that sodium hydroxide gave the clearest supernatant; and, that magnesium oxide gave the most compact precipitate. Constantin and Stockman [23] found that the order of effectiveness in removal of chromium was: calcium hydroxide > sodium hydroxide > ammonium hydroxide > sodium carbonate. The order of filterability of the chromium sludge was found to be: calcium hydroxide > sodium carbonate > ammonium hydroxide > sodium hydroxide. Sodium carbonate proved to be the least effective precipitating agent because of the extremely slow settling rate. One major disadvantage of the use of calcium hydroxide was the formation of large quantities of insoluble calcium sulfate on acidification with sulfuric acid. A matched-sides leather test was used to demonstrate the leather quality effects of blended, recovered chromium-fresh chromium and two stage addition from sodium carbonate precipitated chromium. The final sort for subjective parameters indicated that the test sides were softer than the controls and were equal for hair cell, finish break, veins, and smoothness. The physical testing for stitch tear and grain burst indicated a loss of strength in the test sides [23].

Incineration has also been demonstrated as a method of recovering chromium [24, 25, 26, 27]. Alkaline incineration (pH of 8 to 9, temperatures of 760 to 980 °C), low temperature incineration (pretreatment with sodium carbonate and incineration at 600 °C) and pyrolysis have been investigated and shown to successfully produce soluble chromate. In some cases as much as 25% of the total chromium recovered was in the hexavalent form. The consensus of the investigators was that for leather (trimmings and shavings), incineration was cost effective. The heat value of the leather was required to make the recovery economical. Incineration of sludge alone was not economical.

PROCESS CHARACTERIZATION

Evaluation of the recovery options identified from the literature was performed at a cattlehide tannery producing leather upholstery material. Approximately 18,000 hides per month are tanned in a two-stage batch tanning process. The first stage, which is of primary interest here, involves chromium tanning of the top-grain portion of the hide in wood drums. The second stage uses only vegetable tanning agents.

A process and waste flow schematic for the operations involving chromium at the tannery is shown in Figure 3. The hides are lime split and dehaired prior to being placed in tanning drums. They are rinsed with water and then the chromium tanning solution is added. After reacting with the hides, the tanning liquor is dumped into a pit beneath the drums. The hides are again rinsed and then they and the rinse water are dumped to the tanning pit. The tanning liquor and the second rinse water are pumped from the pit to an in-plant pretreatment facility. The hides are drained and then passed through a wringer to remove excess moisture. The drain and wringer waters are also pumped to the pretreatment facility. The accumulated wastewater is processed on a batch basis by precipitation with sodium hydroxide and flocculation with a polymer.

The waste flow characterization consisted of a series of grab samples collected at the points indicated on the schematic. Liquid, solids and leather

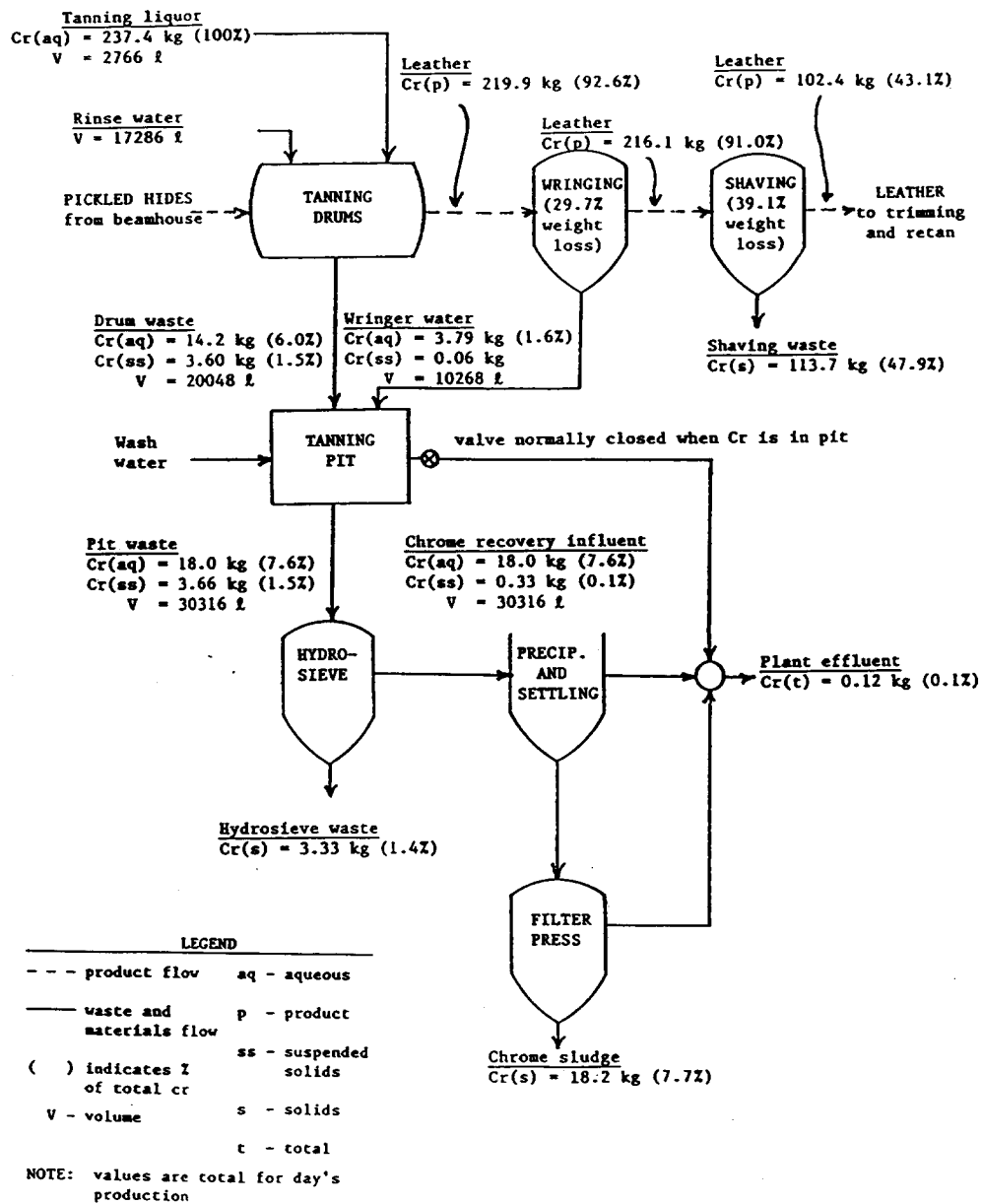


Figure 3. Tannery process and waste flow schematic and chromium mass balance.

samples were taken whenever possible. The solids and leather samples were digested and analyzed for chromium. The liquid samples were filtered, the suspended solids content was determined, and both fractions were analyzed for chromium. Measurements of liquid flow rates, solids generation rates or average weight change in a process step also were taken as needed. Other data was collected from production records, the tanning formula, and discussions with plant personnel.

A complete mass balance was performed for one production day using the collected data. This information is summarized in Figure 3. The results of these analyses revealed that, on a mass basis, the majority of the chromium not fixed in the leather product was in the dissolved fraction of the liquid leaving

the tanning drum. Most of this chromium is removed in the in-plant pretreatment system, and currently leaves that plant as sludge. The other major portion of chromium that does not end up in the finished leather is that lost in the shaving and trimming operations. The loss of chromium in these operations is roughly proportional to the weight loss of the leather.

The wastewater pretreatment process reduced the influent chromium concentration from 690 mg/L to approximately 6 mg/L. The effluent is discharged to the municipal wastewater treatment system, in full compliance with the discharge permit. The influent concentration ranged from 335 mg/L to 1,130 mg/L over the course of a drum dump and clean-up. The lower concentrations were observed during the clean-up operations, while higher concentrations were recorded in the initial samples taken after the tanning liquor dump. Hoses were used to clean the tanning pit. These did not have automatic shut-offs and frequently were left running between dumps. This results in additional volume of wastewater to be treated.

During capacity production, the wastewater treatment facility becomes the limiting factor in the production rate because of the limited storage capacity of the holding tanks. Attempts to speed up the settling rate of the sludge resulted in dosages of excessive amounts of sodium hydroxide. This resulted in an increase in the volume of sludge as well as an increase in chemical costs.

EVALUATION OF POTENTIAL CHROMIUM RECOVERY PROCESSES

Bench-scale tests were used to examine four processes for recovering chromium from the spent tanning liquor: (1) precipitation/dissolution; (2) liquid ion exchange; (3) resin ion exchange and (4) membrane separation.

In the first experiment, a jar test was conducted on the wastewater from the hydrosieve. A pH of 9 was required to reach an acceptable chromium level of 3 mg/L (Table 1). Higher pH's resulted in lower chromium concentrations but also generated substantially greater volumes of sludge. As a part of this experiment, filter cake was dissolved with sulfuric and hydrochloric acid. Acid was added at a ratio of 1:1 on a mass basis. The resulting solutions had chromium concentrations of 720 and 660 mg/L for the sulfuric and hydrochloric acids, respectively. These results are equivalent considering the precision of the sampling and analysis. As expected, the sulfuric acid dissolution resulted in a finely divided precipitate that was difficult to filter.

One ion exchange resin (DOWEX 50W) was examined. For this experiment new samples were taken from the hydrosieve effluent. The starting concentration was 940 mg/L. The resin showed a breakthrough of 105 mg/L within 30 minutes. It was exceedingly difficult to regenerate the column. The volume and concentration of acid resulted in a solution that was the same as the influent, i.e. no concentration was accomplished.

A proprietary packaged treatment system manufactured by Devoe-Holbein was examined. Tests were performed using a bench-scale system provided by a company representative. The test results using a filtered sample of the spent liquor at

Table 1. Sodium hydroxide precipitation of chromium tanning wastewater.

Jar Number	pH	Chromium Concentration, mg/L	Sludge Volume, mL
1	6.1	24	ND
2	8.2	14.5	450
3	9.1	2.7	590
4	10.5	3.0	1,375
5	11.1	0.55	1,350
6	12.1	0.20	1,350

Table 2. Devoe-Holbein treatment of chromium tanning wastewater.

Run Number	Influent Concentration, mg/L	Effluent Concentration, mg/L
1	940	510
2	940	780
3	940	780
4	940	780

pH 4 are shown in Table 2. It is obvious that this was not satisfactory from either a treatment perspective or a recovery perspective. Problems were also encountered with fouling of the system by small particles not removed in filtering. Since the system is designed to release the removed metals by an acid rinse, it is possible that the poor performance was a result of the low feed pH. Treatment of samples that had the pH increased with caustic was not attempted due to the formation of a hydroxide precipitate which would only aggravate the fouling problems.

Acid extraction of the shavings was also evaluated as a potential chromium recovery process. Shavings samples were placed in polyethylene bottles with varying concentrations of sulfuric acid in a 1:5 weight ratio (shavings:acid solution) and shaken for 24 hours on a reciprocating shaker. The results of this test are shown in Table 3. Using 100% acid, approximately 30% of the chromium in the shavings could be recovered in this manner, resulting in an concentrated acid solution containing up to 4460 mg/l chromium. This process is not likely to be cost effective by itself since over 400 pounds of acid would be required for each pound of chromium recovered. Alternatively, sulfuric acid and chromium salts are both being added in the tanning process, such a technique might be employed to reduce the amount of chromium added. It is questionable, however, whether this reduction would offset the cost of the extraction procedure. An additional consideration is whether the high levels of organics that are solubilized in the procedure would interfere with the tanning process.

Table 3. Acid extraction of chromium from shaving waste solids.

Acid Concentration, %	Chromium Concentration, mg/l	Recovery, %
0	43	0.5
2	880	10.7
5	1190	14.1
10	1450	16.5
25	2190	22.4
50	3220	28.0
100	4460	29.8

CONCLUSIONS

Characterization of the tanning process revealed that, on a mass basis, a majority of the chromium that is lost from the process is lost in the liquid fraction as soluble chromium. The volume of wastewater can be reduced by improving housekeeping practices. This would result in a higher concentration of chromium in the waste treatment facility influent and, hence, improve the economics of recovery.

Only two schemes to recover chromium from the tanning liquor appear to be technically feasible. The first is direct reuse of the chromium liquor after filtering and reconstitution as suggested by Davis and Scroggie [7-12]. Although evaluation of this approach was beyond the experimental scope of this work, it appears to be the most economical and least complex in terms of physical/chemical operations. In considering this approach, attention should be given to reducing the extent to which this liquor is diluted. This could be accomplished by changes in the procedures for emptying the drums and rinsing the tanning pit. In addition, more tanks may be required to implement this alternative to allow for blending, quality control checks, etc.

The second waste liquor recovery scheme is the precipitation/dissolution technique. Hydrochloric acid is better than sulfuric acid because it does not form a precipitate. It appears that virtually all of the chromium that is precipitated may be recovered. However, the concentration at which it is recovered is not any greater than that of the incoming wastewater. This implies that direct recycle (with reconstitution) is the more efficient and cost effective method. It is also obvious that the higher the concentration of chromium in the wastewater the better. Good housekeeping practices to reduce the water volume are important to the economics of either recovery process.

There also appear to be two technically feasible schemes for recovery of chromium from the solid waste streams. The first is acid extraction, but it is doubtful that this is cost effective. Furthermore, the technique only removes approximately 30% of the chromium from shaving waste and is likely to be even less efficient with scraps. This leaves a residue that is still high in chromium, acidic, and thus is likely to represent even more of a disposal problem than the original solids.

The second possibility is incineration. While the economics of this depend somewhat on size, it should be noted that a number of smaller, efficient incinerators have become available in recent years. Adding to the cost, however, is the need for relatively sophisticated air pollution control equipment to minimize the emissions of hexavalent chromium. If tanning sludges become classified as hazardous wastes, this may become a cost-effective alternative for sludges, shavings and scraps. This option has the additional advantage that by ending the use of land disposal, a company would reduce its potential liability. It should be noted, however, that this involves handling hexavalent chromium which may increase its potential liability.

ACKNOWLEDGMENTS

This work was supported in part by the Eagle Ottawa Leather Company and by the Michigan State University Industrial Development Institute. The authors express their gratitude to David Filipiak and Christopher Young for contributing to the laboratory studies, and to Lowell Rasmussen for his assistance at the tannery.

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Address reprint requests to:
Thomas C. Voice
Department of Civil and
Environmental Engineering
Michigan State University
East Lansing, Michigan 48824