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Utilization of Leather Scraps in Fertilizer Production

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Abstract

This study applies a new method for utilizing wasted leather scraps after chrome and vegetable tanning. It was found that alkaline hydrolysis with high pressure results in the production of fertilizer solution with N content up to 2.8% and Cr(III) amount lower than 1000 ppm. The method is actually applied.

Keywords: leather scraps, utilization, fertlizers, chromium

Introduction

The production of shoes, leather goods and leather tanning processes produce wasted leather scraps whose quantity in Poland is estimated to be 15-20,000 tons per year. Over 90% of these are scraps after chrome tanning, 5-6% after chrome-vegetable tanning, and the rest after vegetable tanning. All these scraps are classified as I-st category hazardous waste.

A typical scrap has an area of 1-10 cm^2, moisture averages 30-60%, and bulk density, which depends on moisture content, is 1200-1600 kg/m^3. Leather scraps after chrome tanning are waste scraps from shoe and fancy goods production containing up to 12.5% N, up to 2% of fat, 3.5-5% of Cr(III), over 30% H_2O, and tanning solid wastes (after slimming and trimming) containing up to 12.5% N, up to 2% of fat, 2-5% Cr(III) and up to 70% H_2O.

Leather scraps after chrome-vegetable tanning contain up to 1% Cr(III), 7-9% N and up to 10% fat. Scraps after vegetable tanning contain up to 7% N and 7-20% of fat. Moisture of both mentioned types is similar at level 30-60% [1]

All leather scrap utilization technologies are based on the hydrolysis process of fibrylar keratin from scleroproteine group. Keratin is insoluble in water, diluted acids and bases and it has low hydrolysis susceptibility. Tanning processes reinforces protein structures, therefore only high pressure and high temperature hydrolysis could partially destroy keratin structure [2].

Until now only 30-40% of leather scraps after only chrome tanning have beed utilized into fertilizing leather powder using the "semi-dry" method.

Batch "semi-dry" process of hydrolysis at temperatures up to 423K and under pressure up to 0.5 MPa during 2 hours is realized in autoclaves and results in 60% hydrolysis of total proteins. Produced leather powder contains up to 12.2% N_{total} ($N_{digestible}$ – up to 7.3%), fat to 4%, H_2O to 7%, Cr(III) up to 3.5%. Total proteins content was 76% (in this up to 46% digestible proteins) and ratio N/Cr = 5.5. Produced leather powder has bulk density 1600 kg/m^3, granulation 70% between 0.5-1.5 mm and 28% below 0.5 mm.

Fertilizing leather powder is used as raw material for flowers and grass fertilizer production.

The basic problem of this technology are wastes. The "semi-dry" method generates 1.5 m^3 of waste per ton of product containing 0.6-1 g/dm^3 of Cr(III) [3,4] and organic compounds. Some of these waste treatment methods have been implemented [5]. The flow diagram of this method is presented in Fig.1.

Another problem is low product quality connected with high concentrations of Cr(III) resulting in a low N/Cr ratio of from 3.5 to 6, which should be much higher. Chromium content in the product is decreased down to 2%. Only some parts of leather scraps after chrome tanning, containing less than 4% of Cr(III) can be utilized with semi-dry technology. It isn't possible to utilize in this process scraps after chrome-vegetable and vegetable tanning. Experiments in this field have not resulted in any significant progress.

Research carried out during the last 15 years could develop new utilization technologies for turning all types leather scraps into fertilizers.

In 1987-1989, the "dry" wasteless method of leather powder production was worked out [6, 7], which was not implemented due to of high costs and unsatisfactory product quality. In this method, two stage process is realized in rotary autoclaves of special construction. Cr(III) content in this method (lower than 1.8%) was too high and N/Cr ratio (5-7) still too low.

Solving these problems required basic research of leather scrap hydrolysis [2, 4]. First, the possibility of hyd-

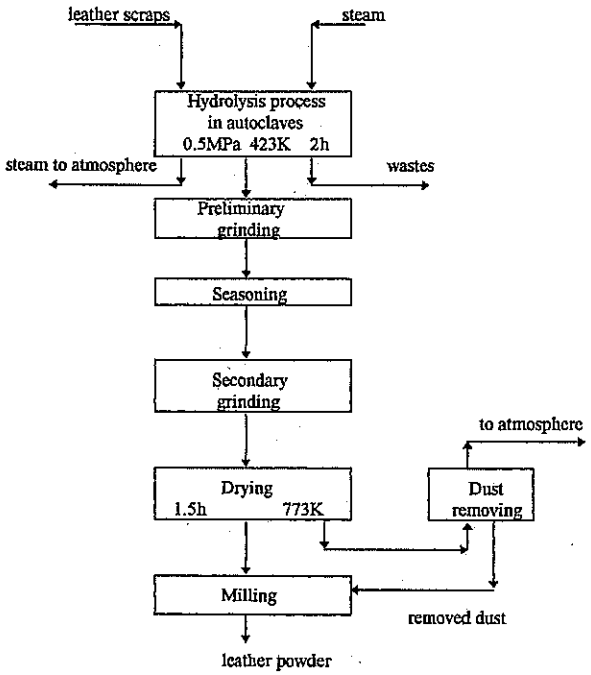


Fig. 1. Flowsheet of the "semi-dry" method of leather scrap utilization into fertilizing "leather powder".

rolysis at normal pressure with water containing acid or hydroxide was examined [2]. Results suggest that a new solution may be hydrolysis with higher pressure [2, 7, 8].

Experimental

Experiments were carried out on leather scraps after chrome tanning containing 2-4% Cr(III) and 35-45% humidity in a laboratory autoclave V = 10 dm^3 with mixer.

In the investigation we used NaOH solution with concentration 1-4% NaOH. The relationship of scraps to water was from 1:1 to 1:3 by weight. Hydrolysis time was from 2 to 4 hours. Steam used in hydrolysis brought directly into the autoclave had a pressure of 1-1.5 MPa and temperature to 473 K. Wasted gases after hydrolysis were absorbed to

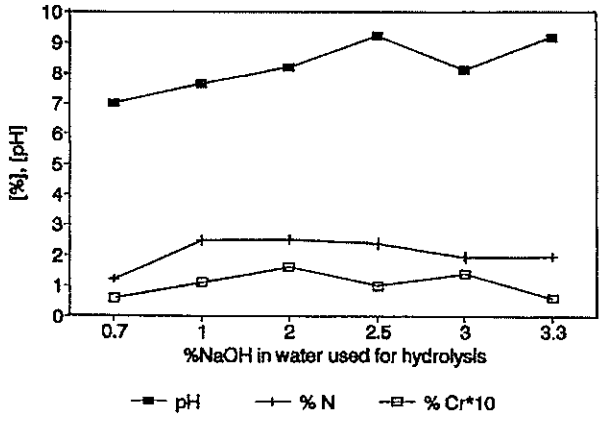


Fig. 2. Relationship of hydrolysis product composition and NaOH concentration.

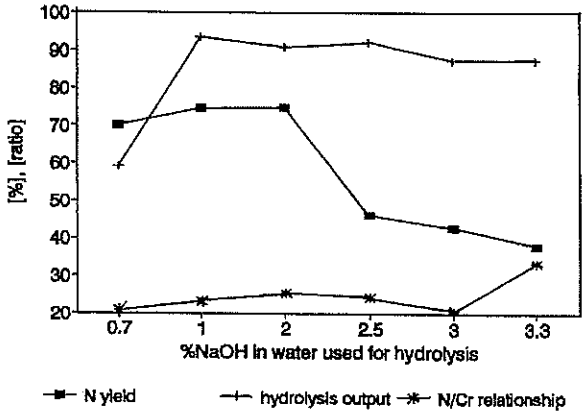


Fig. 3. Hydrolysis output and NaOH concentration relationship.

determine their nitrogen content. Determination of nitrogen and chromium amount in raw material and hydrolysis product allowed us to find nitrogen balance and process output.

This preliminary research formed a basis for more methodical research. Results of the leather scrap hydrolysis process depended on alkalinity of used water; also important was the weight relationship between raw material and NaOH. Results are shown in Figures 2-5.

The concentration of NaOH in water used in hydrolysis reaching 2% was admitted to be advantageous to obtain over 2% of N and less than 1000 ppm of Cr(III) in solution. N/Cr ratio reached 25, hydrolysis output 94%, and nitrogen yield from scraps up to 75%.

The quantity of NaOH consumed per 1000 g of leather scraps up to 40 g was estimated to be sufficient to obtain 2-2.5% N and approximately 1000 ppm Cr(III) in the solution, which had pH to 8-8.5 and N/Cr = 25. Proteins hydrolysis output was over 90% and nitrogen recovery yield from scraps was up to 75%. Waste gases from autoclave absorbed in water contained up to 1% digestible nitrogen. This liquid could be recirculated and used for NaOH solution preparation.

The solution after hydrolysis represented a brownish liquid with disagreeable odor and visible suspension. Total

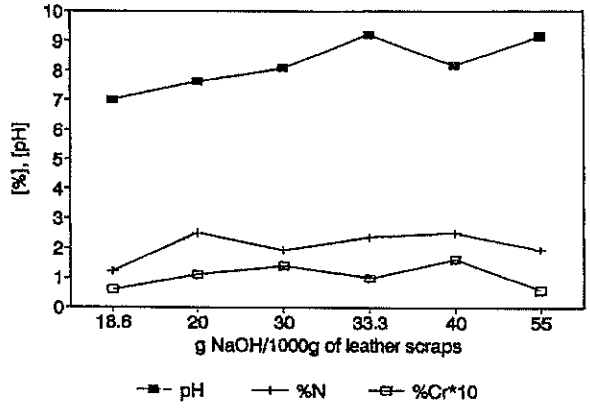


Fig. 4. Relationship of hydrolysis product composition and NaOH quantity.

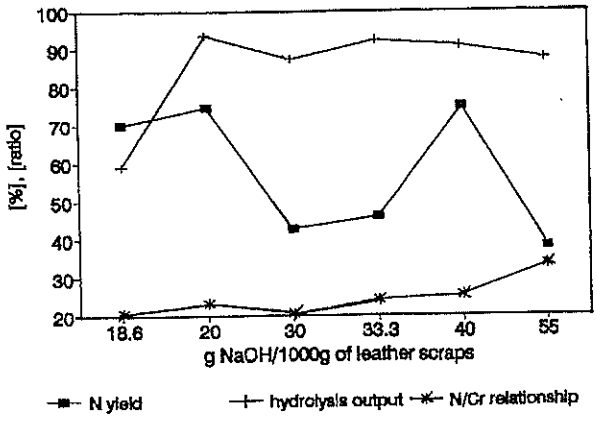


Fig. 5. Hydrolysis output and NaOH quantity relationship.

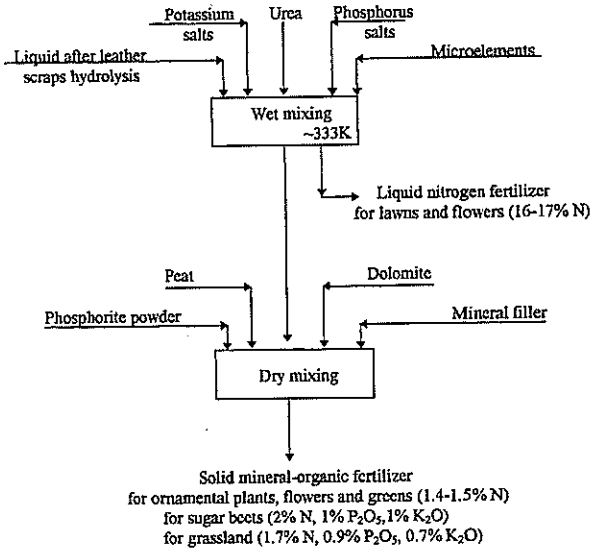


Fig. 7. Flow-diagram of mineral-organic fertilizer production.

suspended solids amounted on the average to 70 g/dm^3. Slurry was filtrated with a laboratory frame press. Filtration rate over 350 dm^3/m^2/h was relatively high.

Flowsheet of the evolved "wet method" is shown in Fig. 6.

Obtained nitrogen liquid will be used as raw material for production of mineral-organic fertilizers (for flowers, greens, sugar beets and others). Some idea of this production is based on mixing raw materials (micro- and macroelements) as in "bulk blending" fertilizer plants. Designed plant should produce up to 12,000 t/y of different types of solid fertilizers and 1000 t/y of liquid nitrogen fertilizers [4].

Flow diagram of mineral-organic fertilizers production from leather hydrolyzate is presented in Fig. 7.

Cake from the filter press contained 13.5-14% Cr_2O_3 and 55-65% H_2O. After drying, Cr_2O_3 concentration was increased to 21% and H_2O concentration decreased to 25%. After calcination during 6h at 473K, the concentration of Cr_2O_3 could be increased to 30%. Calcinated product of this type could be used as chromic ore substitute into sodium chromate production process. Research in this field continues [9].

Conclusions

First industrial trials of leather scraps hydrolysis method were carried out in 1994 with the scale to 3,000 kg of product per 1 charge. Pressure in autoclave was up to 1.5 MPa and hydrolysis time was longer than in laboratory research, reaching up to 8 hours. Industrial trial results were better than these in laboratory scale. Average hydrolysis product contained 2.8% N, 820 ppm Cr(III) and N/Cr relationship was 30. Nitrogen yield from scraps was at 84%. Obtained liquid nitrogen fertilizer will be the base for production of different types of mineral-organic fertilizers.

These results are the basis for a project at a plant with capacity of 10,000 t/y. The first plant has now been erected near Olkusz. The basic flow sheet of this plant was shown in Fig. 8.

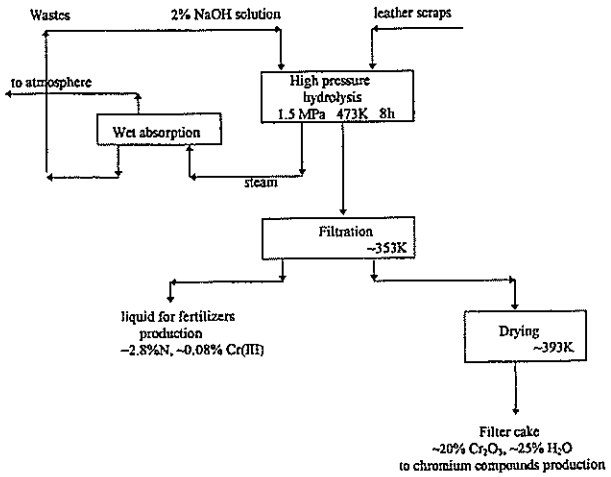


Fig. 6. Flowsheet of the "wet" method of leather scrap utilization.

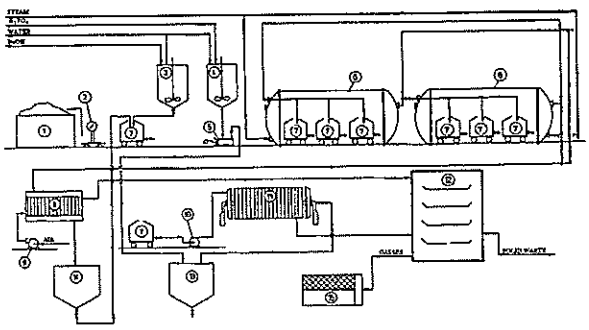


Fig. 8. Flow sheet of leather scrap hydrolysis plant. 1 – leather scrap storage, 2 – scale, 3, 4 – NaOH tanks, 5, 10 – pumps, 6 – autoclaves, 7 – reaction tanks, 8 – heat exchanger, 9 – air fan, 11 – filter-press, 12 – precipitate dryer, 13 – product tank, 14 – condensate tank, 15 – waste gases.

A new method of utilizing leather scraps into fertilizers with high pressure alkaline hydrolysis process should solve the problem of these wastes in Poland. All types of scraps could be utilize with this method. It is simple, cheap and should be profitable for future producers.

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