Research on Resource Utilization of Leather Waste Based on Subcritical Technology

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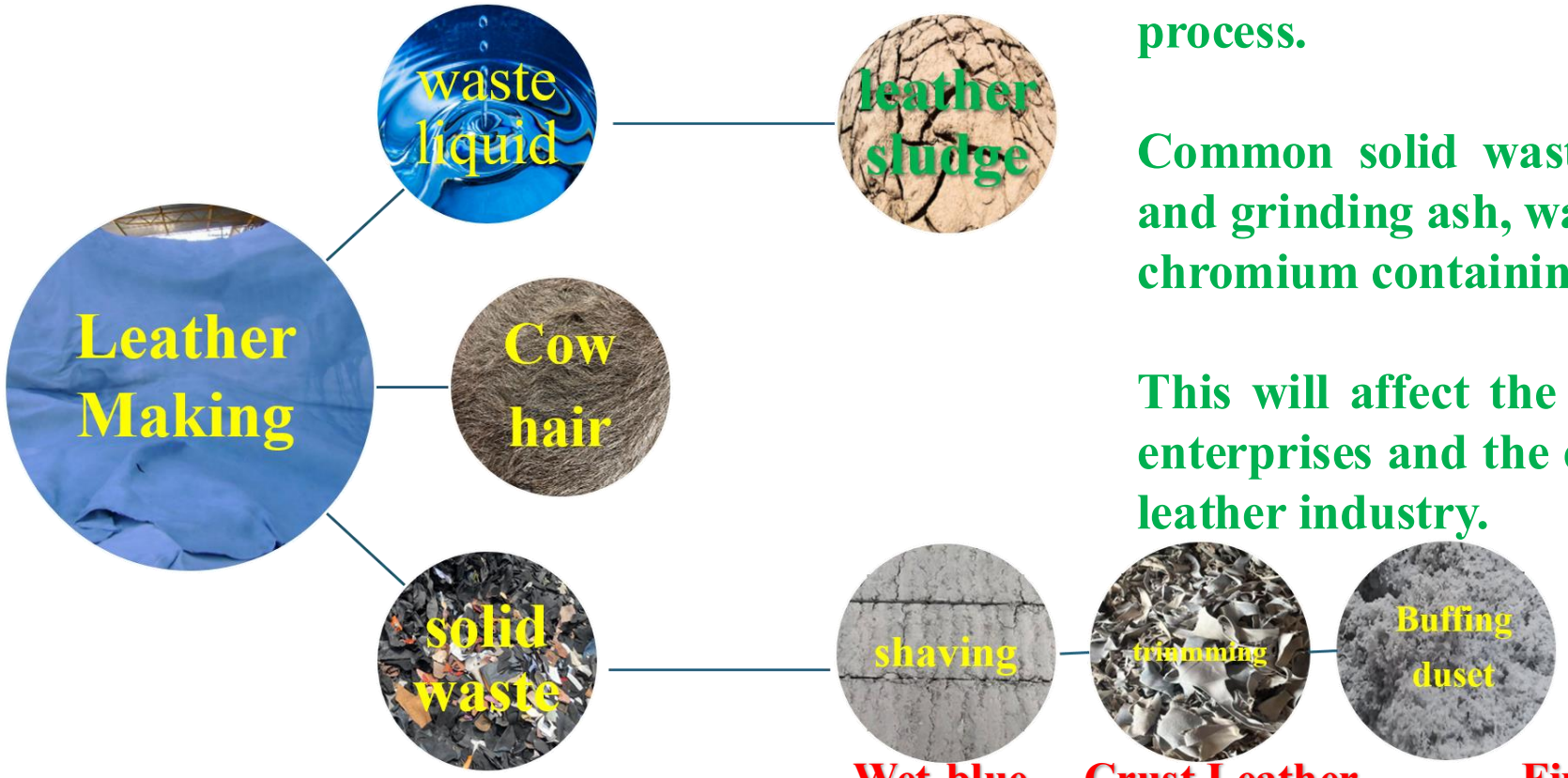
INTRODUCTION

Leather is one of the major industrial sectors facing changes in production and consumption patterns with the rising environmental concerns and societal demands though leather sector utilizes the byproduct (raw hide/skin) generated from meat industry and converts into a value-added product for fashion market.

INTRODUCTION



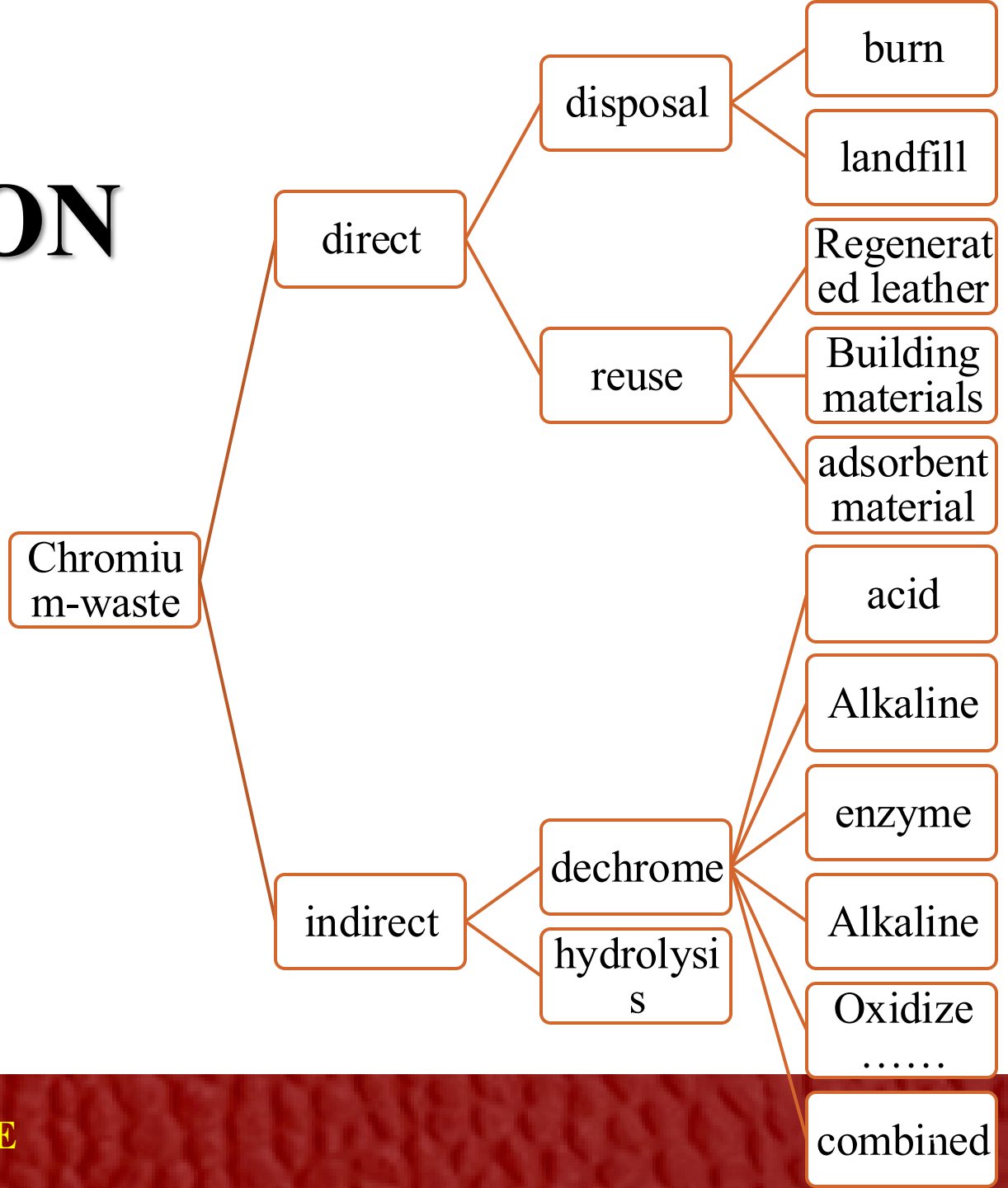
However, waste liquid and solid waste are inevitably generated during the leather making process.

Common solid waste includes shavings, scraps, and grinding ash, waste liquid is treated to obtain chromium containing sludge.

This will affect the economic benefits of leather enterprises and the ecological development of the leather industry.

INTRODUCTION

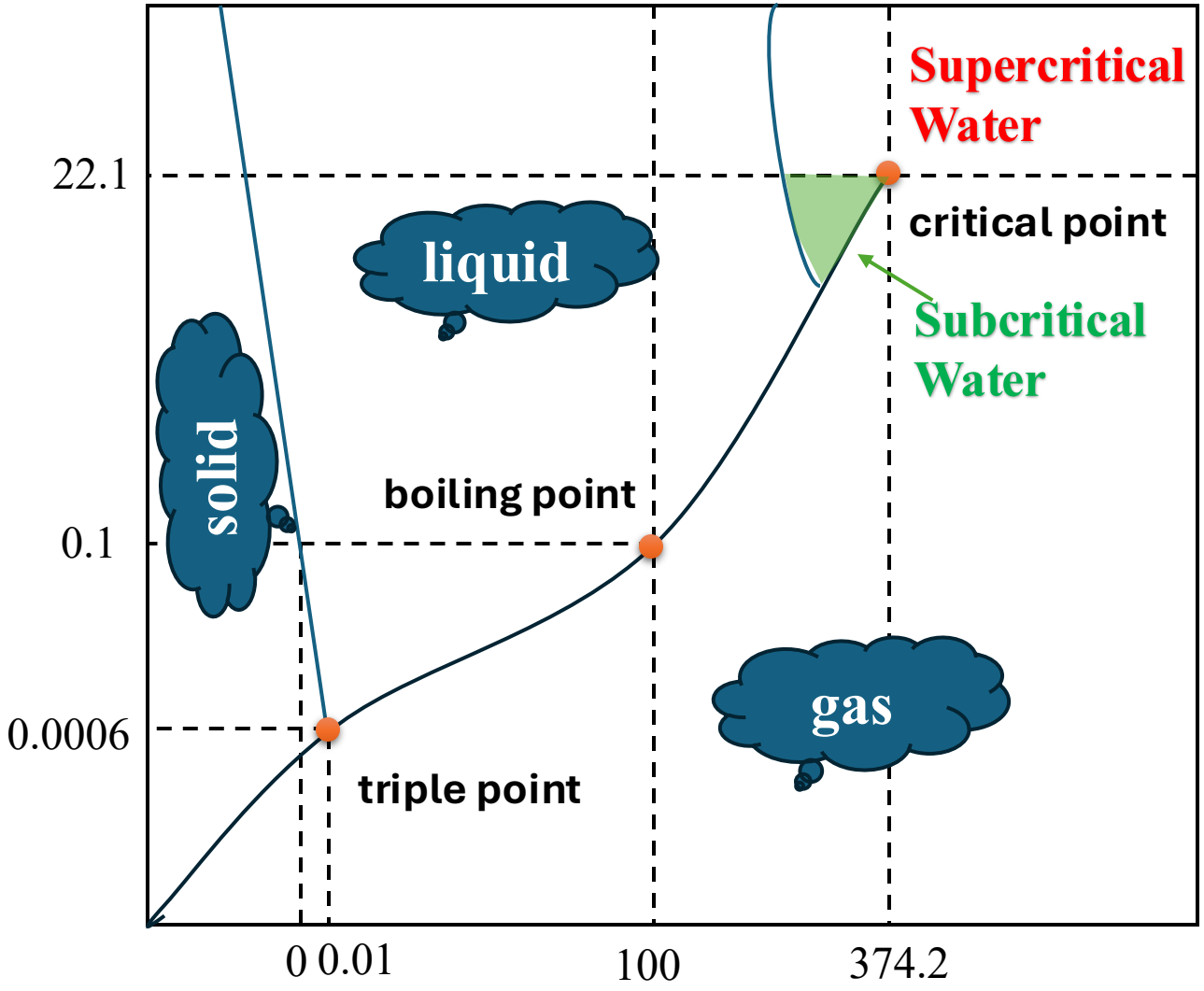
Taking chromium containing solid waste as an example, common treatment methods include burn , landfill , dechrome （Acid, Alkaline, Enzyme, etc） , and hydrolysis, etc. These methods have low utilization rates, high costs, and high pollution, making it difficult to completely solve the problem of waste disposal in the leather industry.



INTRODUCTION

Subcritical Water

liquid state
100-374 ℃
0.1-22.1 Mpa



Here we propose a subcritical water treatment technology.

INTRODUCTION

Subcritical Water

εr：↘

pKw:↘

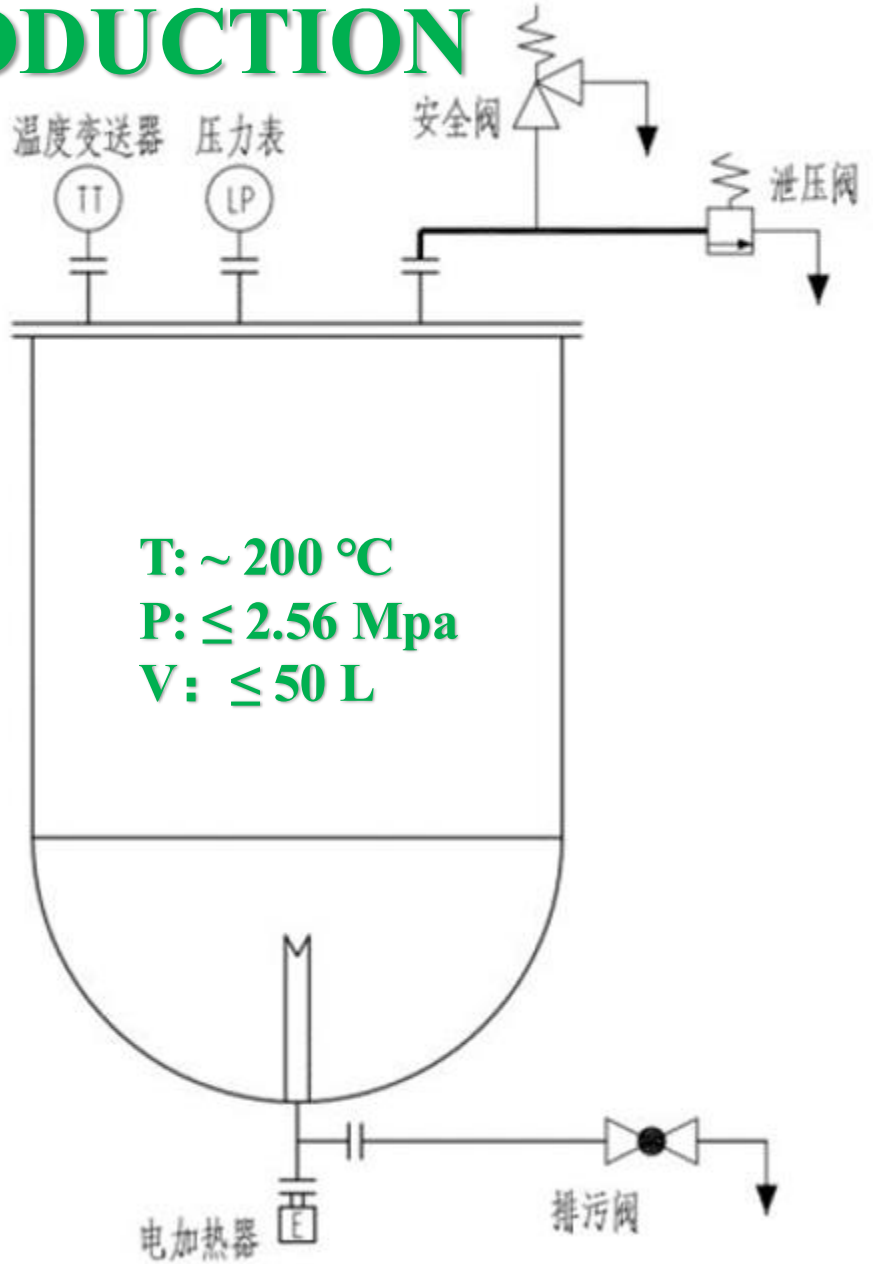
μ:↘

Under high temperature and pressure, rapidly moving hydrogen ions and hydroxide ions in subcritical water constantly collide with chromium shavings molecules, causing the cross-linking bonds between chromium and collagen fibers, as well as the peptide bonds of collagen itself, to be disrupted, resulting in chromium falling off collagen fibers and collagen protein hydrolysis.

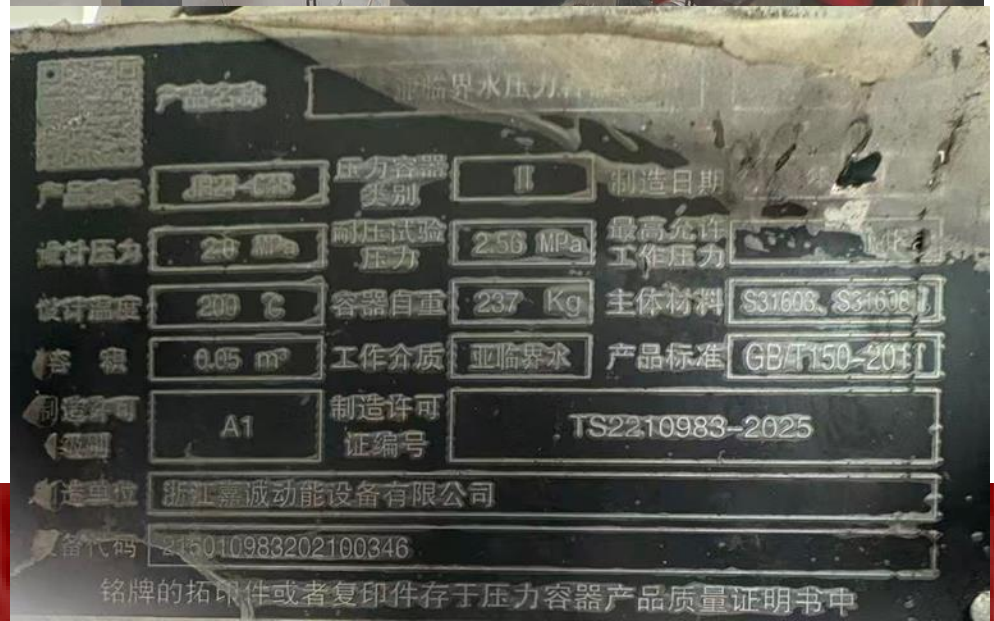
Comparison of characteristic parameters of water at different temperatures

Property parameters		water	Subcritical water	
T（温度）	℃	25	250	350
P（压力）	Mpa	0.1	5	25
P（密度）	g/cm3	1.0	0.8	0.6
εr（介电常数）dielectric constant	F/m	78.5	27.1	14.1
pKw（负对数离子积）Negative logarithmic ion product		14.0	11.2	12.0
c（比热容）	KJ/（kg·K）	4.22	4.86	10.1
μ（粘度）viscosity	mPa·s	0.89	0.11	0.06

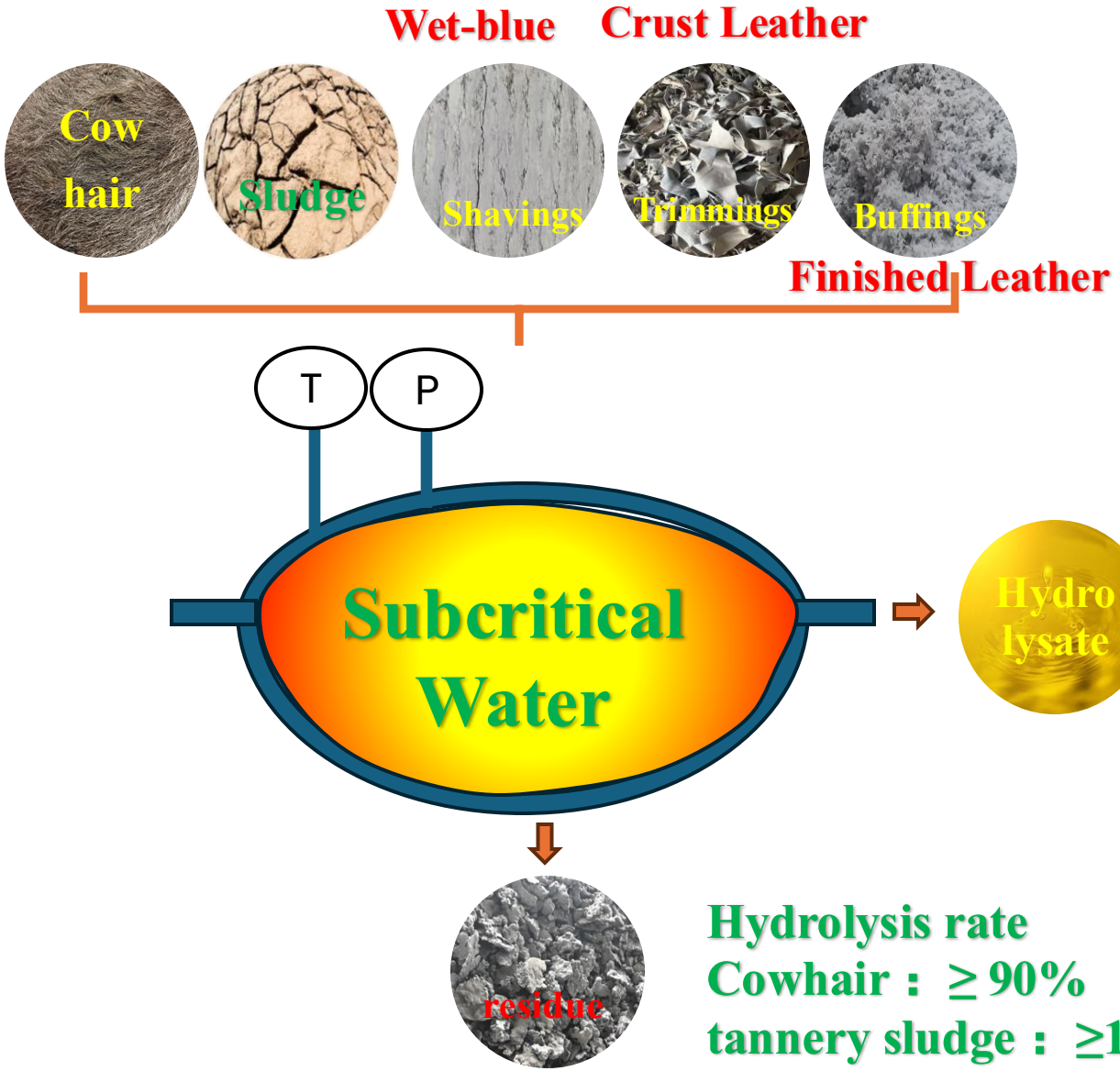
INTRODUCTION



Equipment Design



Experimental Design



Hydrolysis rate
Cowhair： ≥ 90%
tannery sludge： ≥10%
shavings, trimmings, and buffing： ≥ 80%

MATERIAL & METHODS

(CASE: Trimmings)

Material： Trimmings，from the cow crust;
Calcium oxide CaO, supplementary materials;

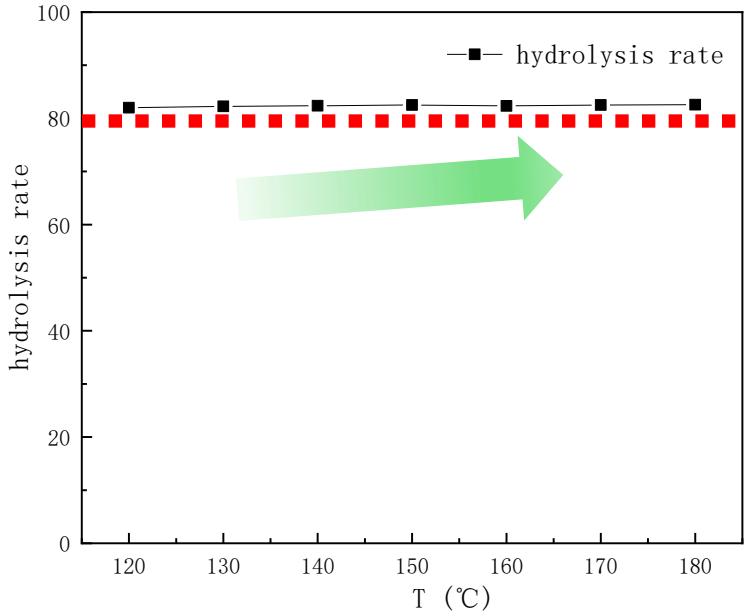
Methods： (1) 30kg of water, 1kg of scraps, 70g of calcium oxide, stir and mix evenly;
(2) Add to subcritical equipment, heat up to 150 degrees Celsius, and then react for 150 minutes;
(3) After cooling, solid-liquid separation yields filter residue (m1) and hydrolysate;
(4) After drying the hydrolysate, the hydrolyzed protein (m2) is obtained;
(5) The hydrolyzed protein (m2) is modified，and used in the leather making.

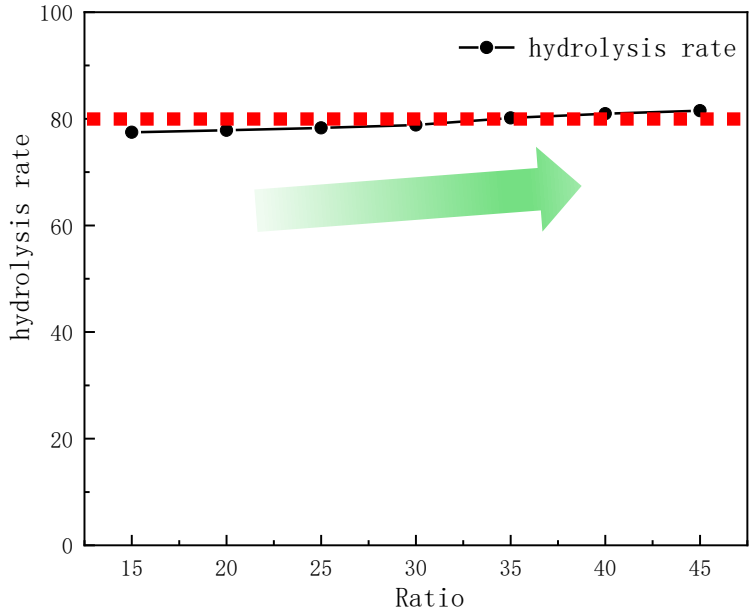
RESULTS & DISCUSSION

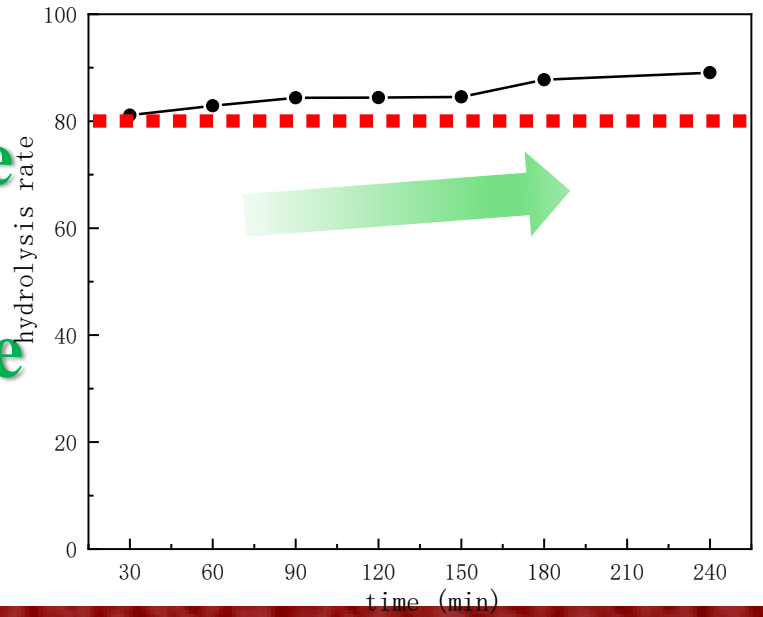
Hydrolysis Rate:

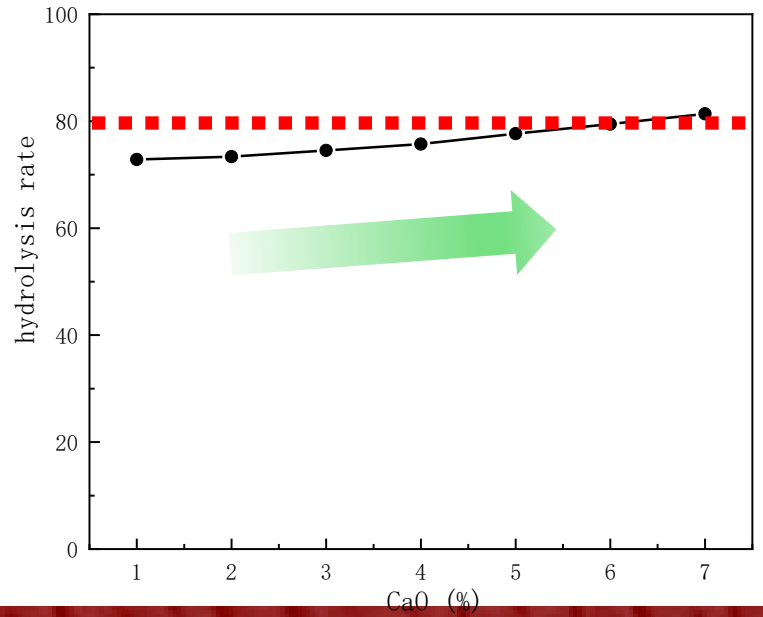
Hydrolysis rate increases with the increase of reaction temperature, time, liquid ratio, and calcium oxide dosage.

The optimal hydrolysis rate is above 80%.



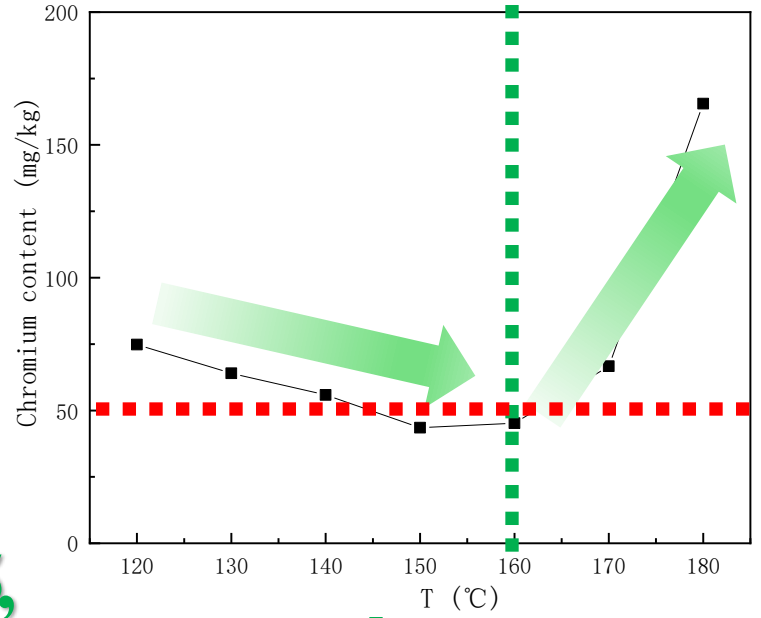


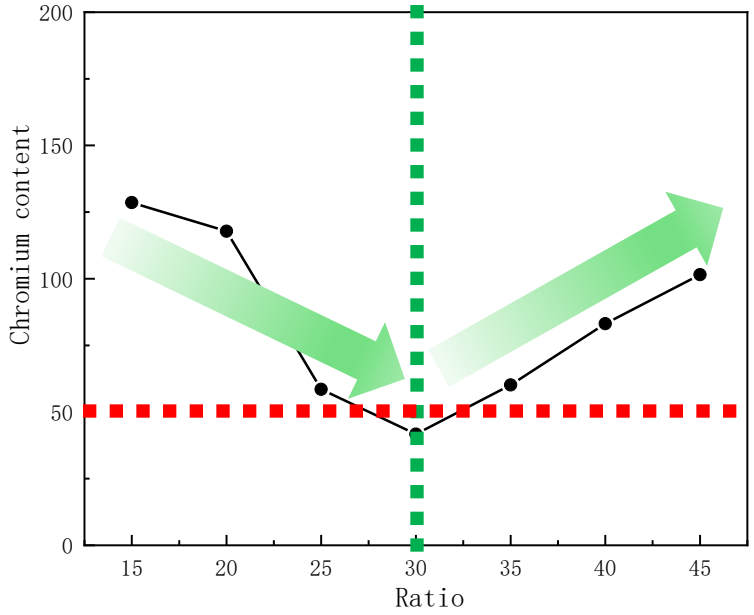


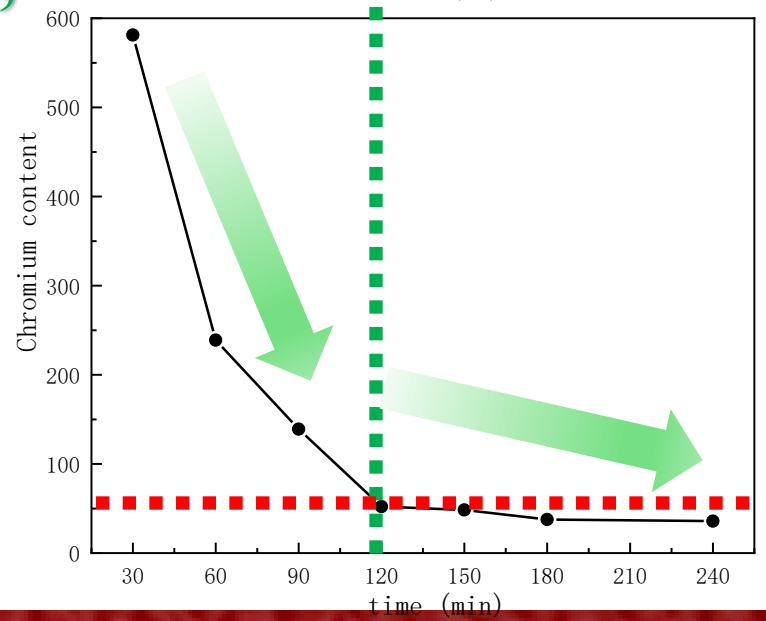


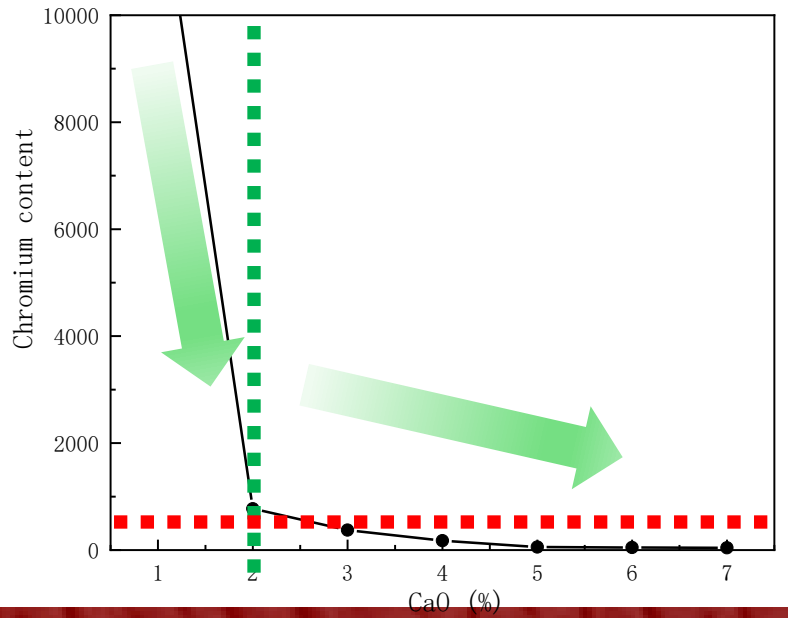
RESULTS & DISCUSSION

Chromium Content:
When the reaction temperature is 140-160 °C, the liquid ratio is 25-35, the reaction time is 2-4 hours, and the amount of calcium oxide is greater than 5%, the lowest chromium content of the hydrolyzed product (dry weight) can be less than 50mg/kg.





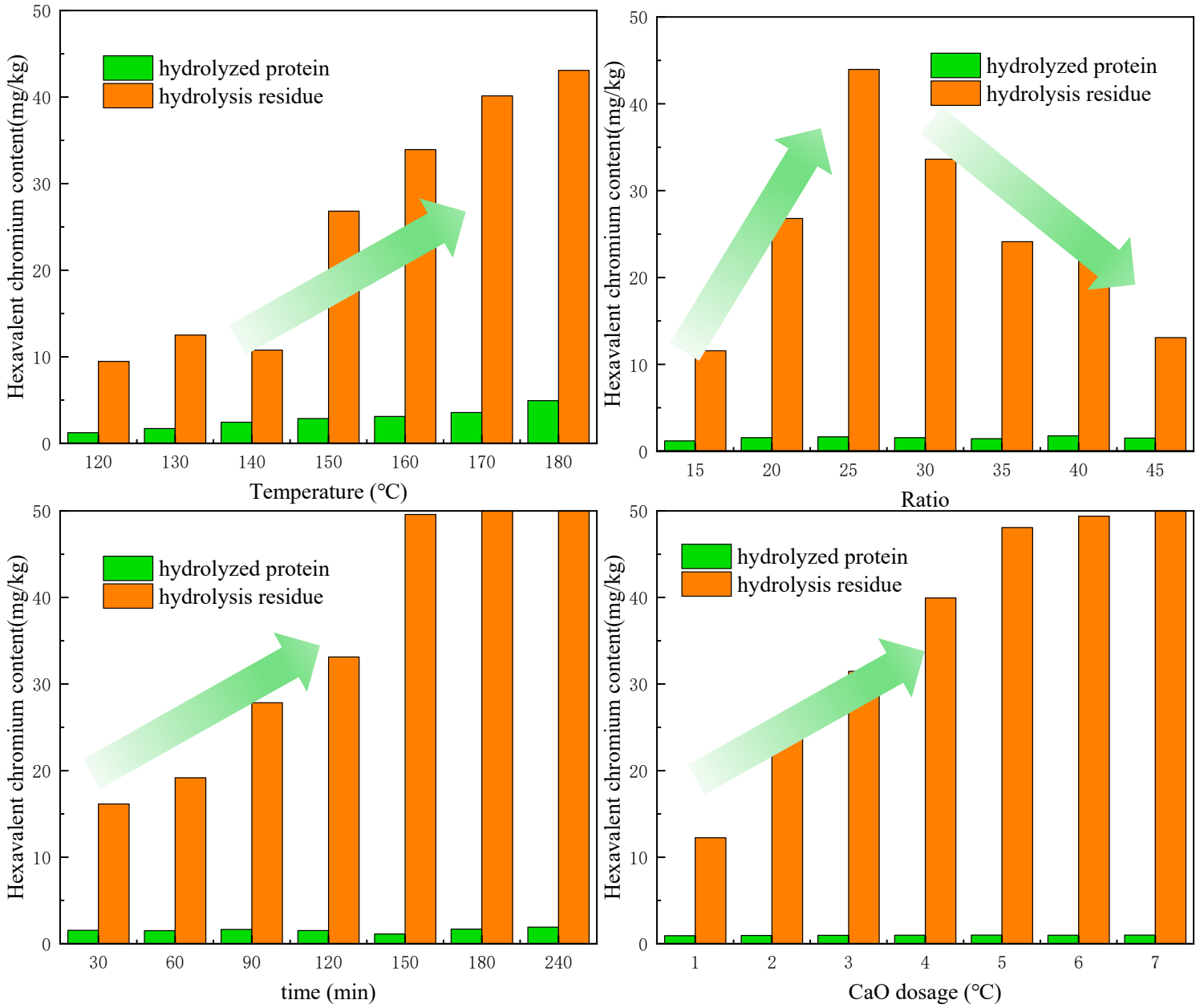




RESULTS & DISCUSSION

Hexavalent chromium content:

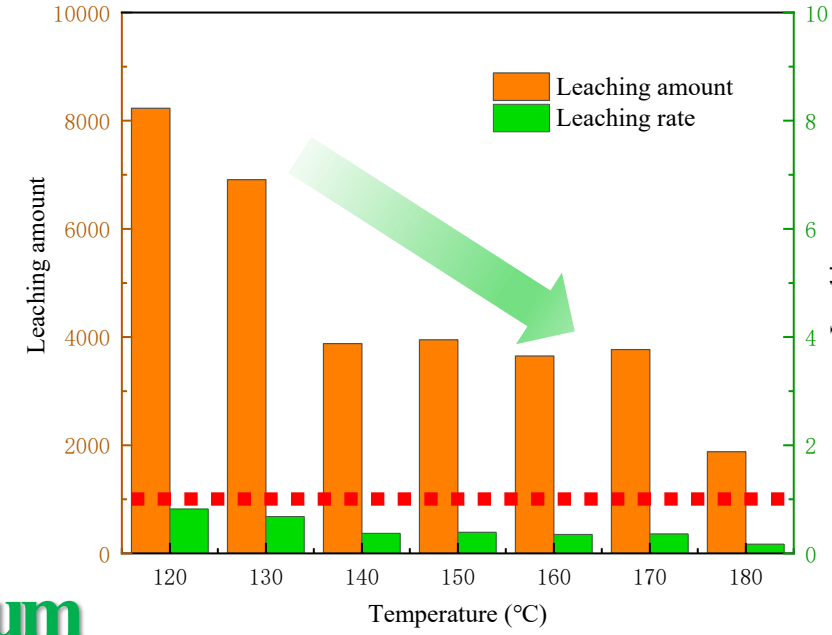
The hexavalent chromium content in hydrolyzed protein is all below 5mg/kg, and the hexavalent chromium content in hydrolyzed residue can be controlled within 50mg/kg. Chromium and hexavalent chromium are mainly present in the hydrolysis residue.

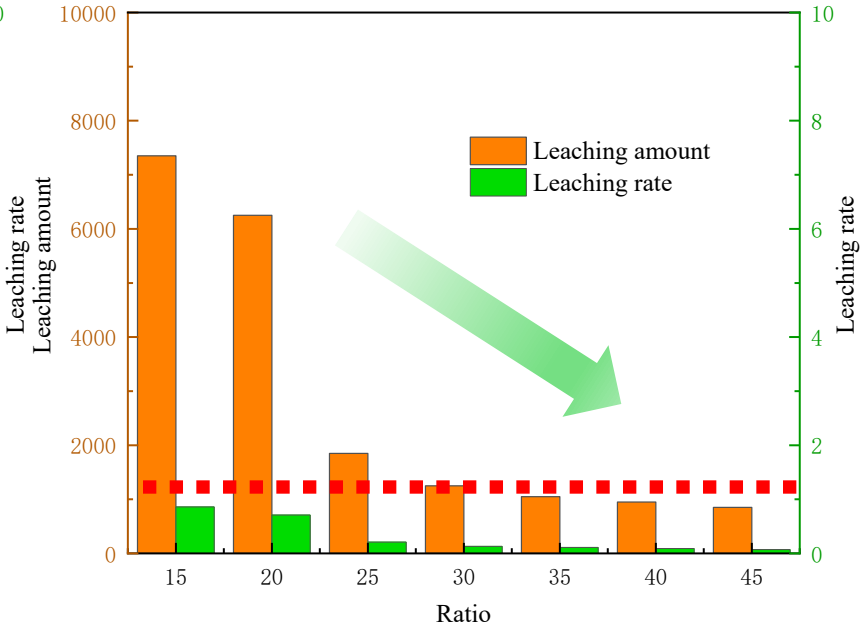


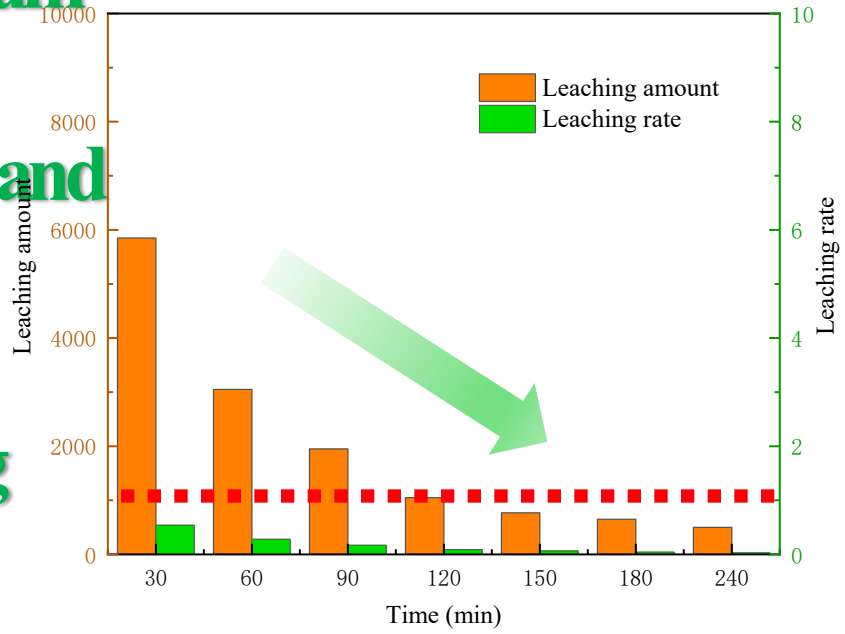
RESULTS & DISCUSSION

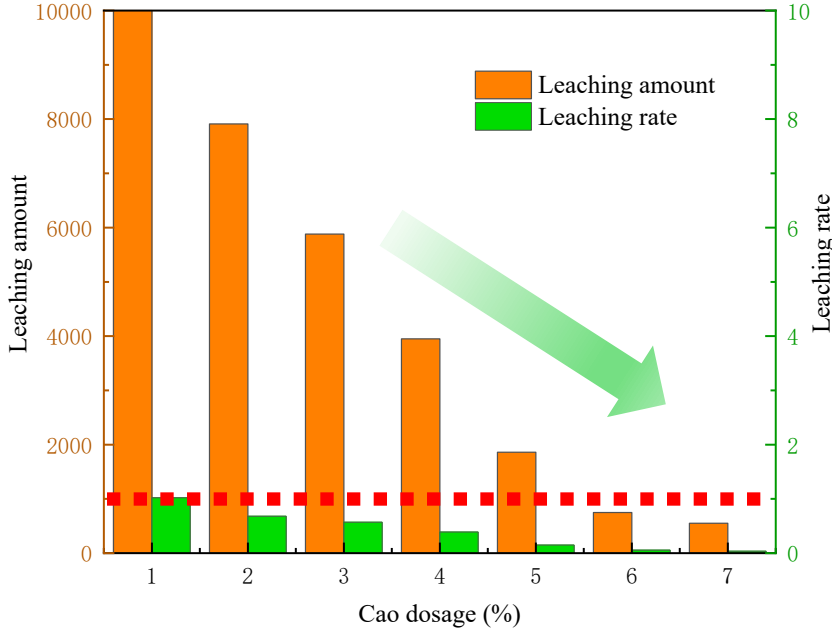
Leaching chromium in residue:

The leaching amount of chromium in the residue is relatively small, generally less than 10000mg/kg, and the leaching rate is generally less than 1%. This indicates that subcritical treatment has a fixing effect on chromium.









RESULTS & DISCUSSION

Orthogonal Design - L_9 (4^3)

Factor - Level	Tem. ℃	Rat. -	Time min	CaO D %
I	150	25	120	6
II	155	30	150	7
III	160	35	180	8

RESULTS & DISCUSSION

Experimental Results:

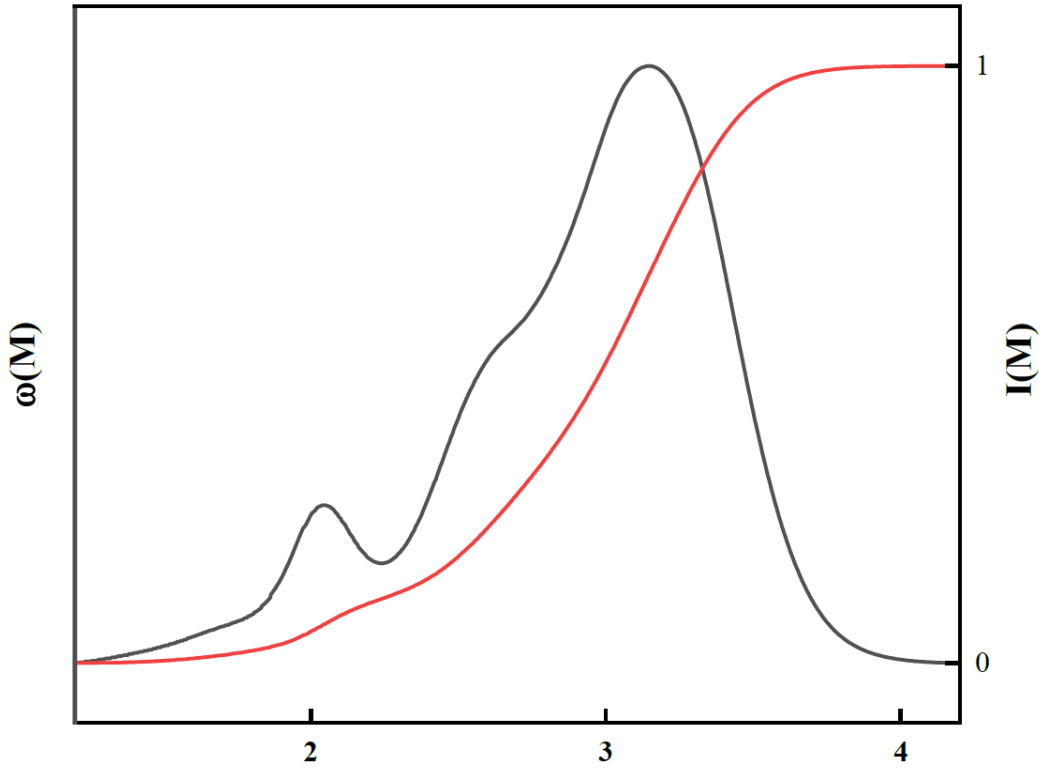
Tem. = 150 ℃
Rio. = 35
Time = 155
CaO = 7%

Index-HA%	Tem. ℃	Rat. -	Time min	CaO D %
K1	225.970	223.854	221.995	224.268
K2	222.895	223.978	225.898	222.648
K3	222.984	224.018	223.957	224.934
R1	3.075	0.164	3.903	2.285
Index-Cr%	**Tem. ℃**	**Rat. -**	**Time min**	**CaO D %**
K1	129.660	137.624	149.414	155.493
K2	140.827	137.959	126.474	143.199
K3	157.947	152.851	152.546	129.241
R2	28.287	15.227	26.072	25.751

RESULTS & DISCUSSION

Hydrolyzed protein

Molecular Weight (Da)	Ratio (%)
≤ 1000 kDa	50.26
≤ 1000-10000 kDa	49.71
≥ 10000 kDa	0.03

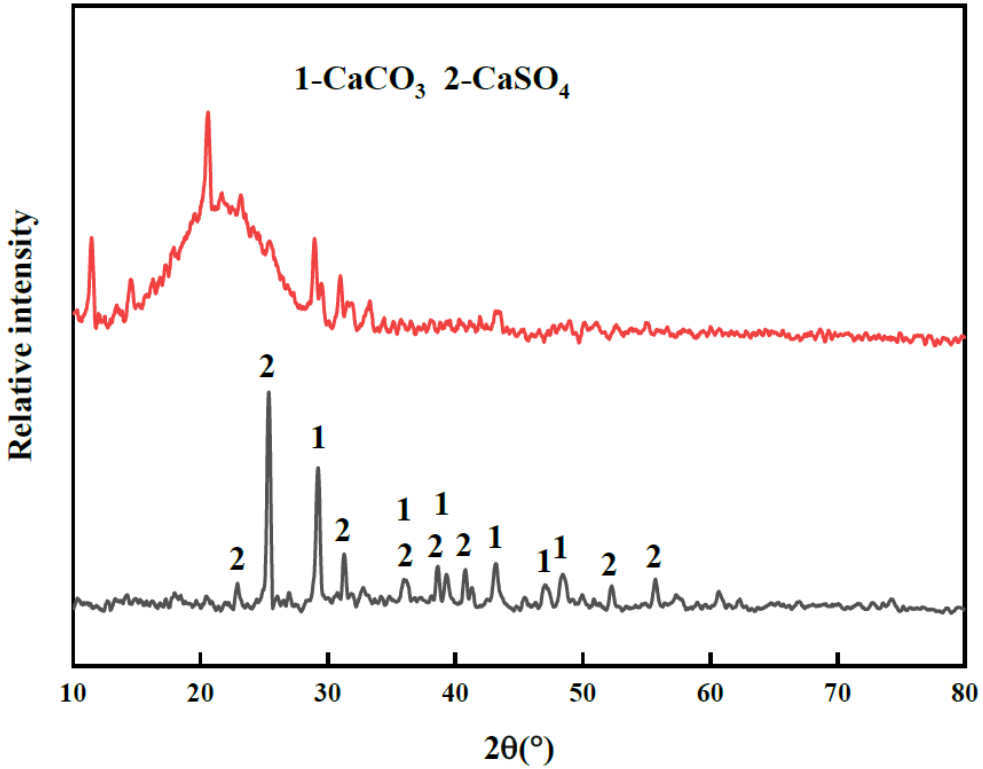


Mw=1321 Mn =407 Mw/Mn=3.09

RESULTS & DISCUSSION

Hydrolysis Residue

Elemental Analysis	Wt(%)
C	21.71
N	2.99
O	42.69
S	9.00
Ca	18.16
Cr	4.11



Possible substances in hydrolysis residue maybe CaCO3, CaSO4, Cr(OH)3.

RESULTS & DISCUSSION

Verification Test Results

Substance	m g	[Cr] mg/g	m Cr g	[Cr(VI)] mg/kg	m[Cr(VI)] mg
Trimmings	1000	25.15	17.55	1.73	1.207
hydrolyzed protein (%)	586.95 (77.68 %)	0.035	0.021 (0.13 %)	1.32	0.773 (12.93 %)
Hydrolysis residue (%)	168.64 (22.32 %)	103.01	17.37 (99.87 %)	30.88	5.207 (87.07%)

HA=81.84% P-Cr =34.81 mg/kg= 0.035 mg/kg

Leaching chromium in residue ≤ 0.0285%

CONCLUSIONS

- ✓ **Hydrolysis：** Subcritical technology can be used on leather waste, achieving weight reduction rates of over 90%, 80%, and 10% for cowhair, trimmings, and sludge, respectively.
- ✓ **Separation：** The hydrolysate is collagen, with a chromium content of less than 50ppm, accounting for only about 0.1% of total chromium.
- ✓ **Fixed：** More than 99% of chromium is present in the hydrolysis residue, but the leaching amount of chromium in the residue is relatively small, generally less than 10000 mg/kg, and the leaching rate is generally less than 1%.
- ✓ We appreciate the equipment and technical support provided by Professor Liu Yan from Sichuan University.

ACKNOWLEDGMENTS