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PhD Thesis

Recycling of Wastes & Thermal Energy Storage

Two Different Ways to Improve Our
Environment

Author
Jaume Cot Gores

Director of the PhD thesis
Dr. Luisa F. Cabeza

Departament d'Informàtica i Enginyeria Industrial
Escola Politècnica Superior
Universitat de Lleida

Recycling of Wastes & Thermal Energy Storage

Two Different Ways to Improve Our Environment

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La Dra. Luisa F. Cabeza, Catedràtica de l'Escola Politècnica Superior de la Universitat de Lleida,

CERTIFICA:

Que la memòria "Recycling of wastes and thermal energy storage, two different ways to improve our environment." presentada per Jaume Cot Gores per optar al grau de doctor s'ha realitzat sota la meva supervisió.

Lleida, 26 de gener del 2012

*Those are my principles, and if you don't
like them...well, I have others*

"Groucho" Marx

*What we know is a drop, what
we don't know is an ocean*

Isaac Newton

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"us estimo"

Summary

The current thesis is a contribution to create energy and resource efficient economy. In particular, the thesis presents, on one hand, the work carried out to treat chromium(III) containing leather wastes and, on the other, the work performed to develop a seasonal solar heat storage system to fulfil the space heating demand and domestic hot water demand of a low energy house during the months without available solar energy.

Conventional treatments to recover solid chromium-collagenic wastes are either time consuming or destroying the original structure of the collagen and, thereby, creating backwards in the way to isolate a high added value of collagenic biopolymers. The current work shows the results for the optimization of a new dechroming process based on the oxidation with peroxides (specifically hydrogen peroxide) in alkaline medium. The oxidation process, followed by washes, reduces the chromium(III) content from 50,000 ppm (original collagen waste) to 20-90 ppm. In addition, recovery and reuse of the chromium(III) present in the chromium(III) -tanned wastes was demonstrated. Moreover, an alternative process to recover tannery-chromium(III) effluents was developed. In this process the same oxidation reaction is applied in order to oxidize completely the chromium(III) present in the effluents to chromium(VI) followed by two sequential steps; a) fixation into a ion-exchange resin and, b) reduction to chromium(III) in a batch combined system. Experimental results show that 97 % recovery can be reached.

On the other hand, chemical adsorption processes and solid-gas chemicals reactions open a new way for long-term solar heat storage in the built environment. The present work gives a review of the experimental research on thermal energy storage systems with thermochemical materials (TCM). Moreover, this work describes the characterisation of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ to determine its suitability for application in a seasonal solar heat storage system. It was found that the amount of water and the energy released by the material turned out to be strongly dependent on the water vapour pressure, temperature, and the total system pressure. Results of this study indicated that the application of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at atmospheric pressure is problematic for a solar heat storage system where heat is released above 40 °C using a water vapour pressure of 1.3 kPa. However, a separate experiment performed in a closed system at low pressure indicated that a small amount of heat can be released at 50 °C and a water vapour pressure of 1.3 kPa. Further experiments were conducted to study the effect of lowering the system pressure on water uptake. Additionally, the salt hydrates of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were also studied as potential TCM. It was found that the chlorides can deliver heat to the residential heating system at a higher temperature than the sulphates.

Resumen

Esta tesis es una contribución a generar una economía eficiente en recursos y energía. En particular esta memoria presenta por una parte, el trabajo realizado para tratar los residuos cromados de la industria del curtido y, por otra parte, el trabajo realizado para desarrollar un sistema estacional de almacenamiento térmico solar que pueda cubrir la demanda de energía para calefacción y agua caliente en casas de bajo consumo energético durante los meses de invierno sin disponibilidad de energía solar.

Los tratamientos convencionales para recuperar los residuos colagénicos cromados (sólido) o bien, requieren mucho tiempo o bien, degradan la estructura original del colágeno y, por lo tanto, imposibilitando la obtención de biopolímeros de alto valor añadido. Este trabajo presenta los resultados obtenidos para la optimización de un nuevo proceso de descromación basada en la oxidación por medio de peróxido de hidrógeno en medio básico. Este proceso seguido de un lavado reduce la cantidad del cromo contenido en el residuo sólido de 50,000 ppm a 20-90 ppm, permitiendo además la recuperación del cromo (III) para su posterior reuso en el proceso de curtido. Por otra parte, la memoria también presenta el desarrollo de un proceso alternativo que permite tratar los efluentes cromados. En este proceso se utiliza también la misma reacción redox para oxidar totalmente el cromo (III) presente en los efluentes a cromo (VI) seguido de dos etapas secuenciales: a) fijación en una resina de intercambio iónico, b) reducción a cromo (III) en una operación combinada de sistemas "batch". Los resultados experimentales han demostrado que es posible obtener una recuperación del 97 %.

Por otra parte, los procesos de adsorción química y las reacciones químicas sólido-gas abren una nueva posibilidad para el almacenamiento térmico de energía solar por periodos largos de tiempo. Este trabajo aporta una revisión al estado del arte sobre la investigación experimental en sistemas de almacenamiento térmico con materiales termoquímicos (TCM). Además, la memoria presenta el trabajo realizado en la caracterización del $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ para la determinación de su aplicación en un sistema estacional de almacenamiento térmico de energía solar. La cantidad de agua adsorbida y la energía desprendida por el material resultaron estar muy condicionadas por la presión de vapor de agua, la temperatura y la presión total del sistema. Los resultados de este estudio indican que la aplicación del $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ a presiones atmosféricas es problemática para el sistema de almacenamiento térmico cuando la liberación de energía se produce por encima de los 40 °C con una presión de vapor del agua de 1.3 kPa. Sin embargo, los resultados de unos primeros experimentos realizados en un sistema cerrado a baja presión indicaron la liberación de una cantidad pequeña de calor a 50 °C y una presión de vapor de agua de 1.3 kPa. Así en un trabajo posterior, se llevaron a cabo más experimentos para estudiar el efecto de un sistema a baja presión en la cantidad de agua adsorbida. En este trabajo también se estudiaron el $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, el $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ y el $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ como potenciales materiales termoquímicos. Se encontró que los cloruros pueden liberar calor al sistema de calefacción residencial a temperaturas más altas que los sulfatos.

Resum

Aquesta tesi és una contribució a generar una economia eficient en recursos i energia. En concret, la memòria presenta d'una banda, el treball realitzat per tractar el residus cromats de la indústria d'adoberia i, d'altra banda, el treball realitzat per desenvolupar un sistema estacional d'emmagatzematge tèrmic solar que pugui complir amb la demanda de calefacció i aigua calenta en cases de baix consum energètic durant el mesos d'hivern sense disponibilitat d'energia solar.

Els tractaments convencionals per recuperar els residus col·lagènics cromats (sòlids) o bé, requereixen molt de temps o bé, degraden l'estructura original del col·lagen i, per tant, impossibilitant la obtenció de biopolímers d'alt valor afegit. Aquest treball presenta els resultats per la optimització d'un nou procés de descromació basat en l'oxidació per mitjà de peròxid d'hidrogen en mitjà bàsic. Aquest procés seguit d'un rentat aconsegueix reduir el contingut de crom en el residu sòlid d'uns 50,000 ppm a 20-90 ppm, permetent a més recuperar el crom (III) per la seva posterior reutilització. D'altra banda, la memòria també presenta el desenvolupament d'un procés alternatiu que permet tracta el efluent cromat. En aquest procés s'utilitza la mateixa redox per oxidar totalment el crom (III) dels efluent a crom (VI) seguit de dues etapes seqüencials: a) fixació en una resina d'intercanvi iònic, b) reducció a crom (III) en una operació combinada de sistemes "batch". Els resultats experimentals han demostrat que es possible obtenir una recuperació del 97 %.

D'altra banda, el processos d'adsorció química i les reaccions químiques sòlid-gas obren una nova possibilitat per l'emmagatzematge tèrmic d'energia solar durant períodes llargs de temps. Aquest treball aporta una revisió a l'estat de l'art sobre la investigació experimental de sistemes d'emmagatzematge tèrmic mitjançant materials termoquímics (TCM). A més, la memòria aporta el treball realitzat per a la caracterització del $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ per la determinació de la seva aplicació en un sistema estacional d'emmagatzematge tèrmic solar. La quantitat d'aigua adsorbida i l'energia despresada va resultar fortament dependents de la pressió de vapor de l'aigua, la temperatura i la pressió total del sistema. Els resultats obtinguts indiquen que l'aplicació de $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ a pressions atmosfèriques es problemàtica per un sistema d'emmagatzematge tèrmic quan la energia alliberada es produeix per sobre dels 40 °C i una pressió de vapor de l'aigua de 1.3 kPa. No obstant això, els resultats d'uns primers experiments realitzats en un sistema tancat a baixa pressió van indicar l'alliberament d'una petita quantitat de calor a 50 °C i una pressió de vapor de l'aigua de 1.3 kPa. Així, en un treball posterior es van dur a terme més experiments per estudiar l'efecte d'un sistema a baixa pressió en la quantitat d'aigua adsorbida. En aquest mateix treball, també es van estudiar el $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ i $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ com a potencials materials termoquímics. Es va trobar que els clorur poden alliberar calor al sistema de calefacció residencial a temperatures més altes que els sulfats.

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1 Introduction

Sustainable chemistry aims to improve the quality and comfort of human life, while reducing the environmental impact of processes and products, optimising the use of finite sources and minimising waste. In this sense, there are many ways in which chemistry and chemical knowledge lead to sustainability, which includes but are not limited to the following:

- In replacing fossil fuels with renewable raw materials for processing and production of chemicals, polymers and energy. This requires development and innovation of the entire life-cycle of the process plants and thereby, covering all areas of chemistry and chemical engineering.
- In improving the current reaction and processes technologies by developing:
 - Novel chemical reactions pathways that for instance reduce the number of reaction and process steps, or that converts industrial waste to alternative fuel and useful raw materials which in turns can be converted into highly value compounds
 - Novel catalysts that allow, for example, accelerate the reaction, milder the reaction conditions and obtaining high yields and selectivities, or that enables for an easy separation and recovery; therefore, reducing the energy consumption and the formation of by products
 - Alternative solvents to organic solvents that are environmental benign such as solvent-free processes, water, supercritical fluids and ionic liquids.
- In energy storage, transport and conversion by means of developing for instance phase change materials, reversible thermochemical reactions or reversible electrochemical reactions. In this sense the energy efficiency of industrial process, power plants and renewable energies can be increased by means of converting waste energy into usable energy.

The current thesis focus on developing chemical reactions capable to lead to sustainability by way of converting waste into highly value biocompounds and waste heat into usable energy.

1.1 Recycle of wastes: Tannery Industry

Over the past decades, sustainable policies have been put into practice to create energy and resource efficient economy, and thus separate waste generation from economic growth. The EU's waste management policy introduced a five-step waste hierarchy where prevention is the best option followed by re-used, recycling and other forms of recovery, with disposal such as landfill as the last resort. EU waste legislation aims to move waste management up to the waste hierarchy (Figure 1.1) [1,2].

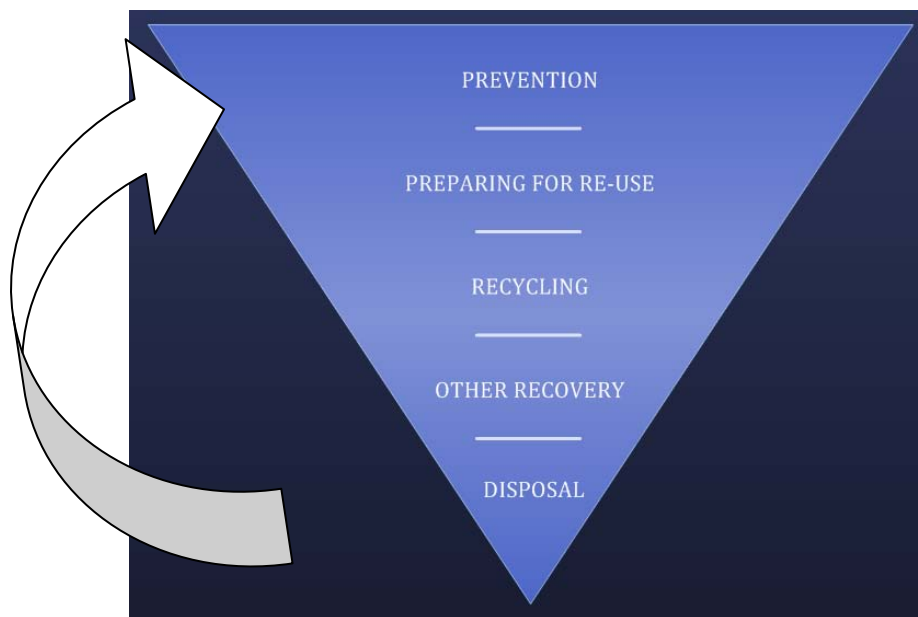


Figure 1.1: Moving up the waste hierarchy [1]

Many productive sectors in Spain, Europe and worldwide are making a real effort to invest in facilities and processes. Examples include, but are not limited to: installing effluent treatment plants (physical-chemical, biological, biomembrane reactors, reverse osmosis, etc.), replacing conventional manufacturing processes with others that use what is known as “clean technology”, trying to process solid waste materials. However, there is still a long way to go in this field.

Waste generation is an important problem for the leather tanning industry. Although, the leather tanning industry's raw material are skin and hides, which is a waste material from the meat industry, their transformation into leather generates large amounts of liquid waste and tanned and non-tanned solid collagen wastes. Figure 1.2 shows a waste flowchart for the leather tanning sector without including the atmospheric pollution generated [3].

kk

In addition, a particular problem for the waste management in the leather tanning industry is that 95 % of it uses chromium(III) salts as a stabilizing agent (crosslinker). Traditionally, land application and disposal of solid, chromium-containing tannery wastes has been widely practiced during most of the twentieth century. This is a rather expensive and environmentally inappropriate way of handling a waste material that has the potential for utilization [4].

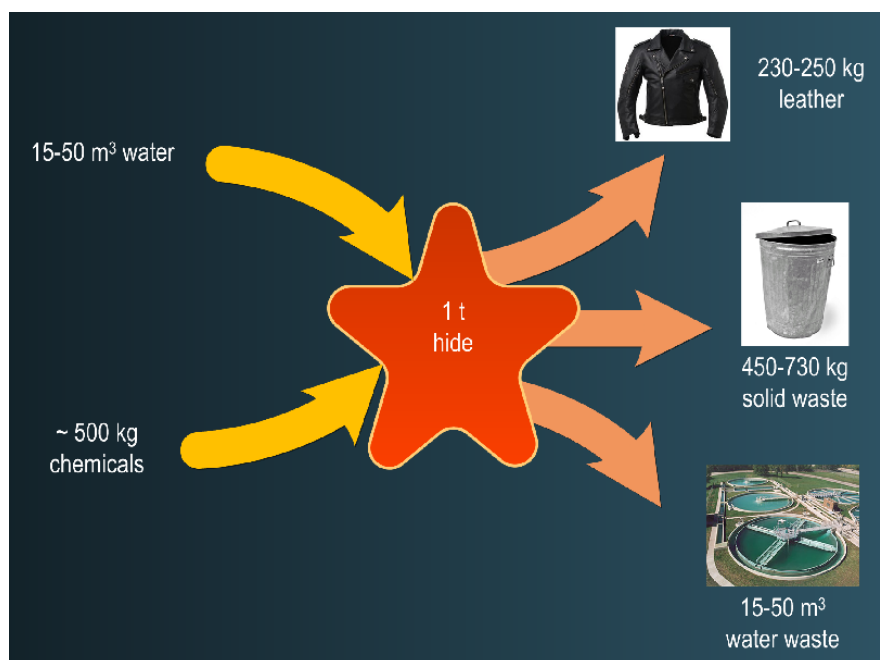


Figure 1.2: Waste flow diagram for the leather industry

Because of the collagen content, recycling this solid waste material would open a wide range of potential applications in the fields of leather, textile, paper, wood, and even might be in the fields of pharmacology, cosmetics, veterinary science, medicine, etc. However, conventional treatments, either are time consuming or degrading up the original structure of the collagen and, thereby, creating a real backward in the way to isolate a high added value of collagenic biopolymers. Moreover, chromium(III) waste causes particular problems, since under current European legislation the accumulation in approved landfills of waste materials containing chromium(III) is forbidden. This is because, depending on the length of time, temperature, pH, microorganisms, etc., some of the chromium(III) may be oxidised to chromium(VI). Chromium(VI) is highly toxic and pollutes the ground and groundwater. Therefore, researchers and tanners are now focused in not only obtaining bioproducts but also to “physically” remove chromium(III)-tanned waste from tanneries, separate inorganic compounds and/or potentially toxic compounds, and gain financial benefits from obtaining industrially reusable bioproducts.

1.1.1 Skin and hides

Skin and hides are the outer covering of mammals, which is used as raw by-product from the meat industry for the manufacturing of leather. In the leather industry, the term hide is used to denote the skin of large animals, such as full grow cattle, steer etc., while, the term skin is used when referring to small animals, such as sheep, goats, calves, etc.



The skin has several important physiological functions that includes, but are not limited to, the following:

- Protects against physical and bacterial damage.
- Contains sensory receptors (nerve endings) that inform about temperature, pressure, touch, etc.
- Helps to control internal temperature.
- Restricts water loss.
- Excretes body wastes.

Of the major functions of the skin, that of protection is the most significant with regards to the physical characteristics of the finished leather.

1.1.1.1 Structure of the skin

Although, the generic structure of the skin is common for all mammal species (Figure 1.3), there are some differences. Some animals are protected primarily by heavy coating hairs and others by denseness of the network of fibres of the skin itself. In addition, the structure of the skin or hide can vary between animals of same species depending upon the habits of life of the animal, season of the year, age, sex, and breeding [5].

The basic structure of mammalian skin can be divided into three main components: (1) epidermis, (2) dermis, and (3) hypodermis.

Epidermis [5-7]: is the outermost layer of the raw skin, and consist mainly of keratiocytes, cells that make the waterproof protein keratine. The deep epidermal layers continually produce new keratinocytes by mitotic cell division that displace, older cells upwards the skin's surface. As cells move upward, they become flattened and eventually die. The dead cells at the skin surface are gradually sloughed off.

The epidermal system also includes mainly the hair and wool. The hairs and wool are placed in the hair follicle, which project downward into the dermis. At the bottom of the hair follicle there is direct connection between the bulbous root of the hair and the blood-vessels. In addition, the epidermal system contains sweat glands, which discharge sweat through the pores of grain, and oil glands, which keep the skin and hair soft and silky. The hair follicles, sweat glands and oil glands are made up of epidermal cells that migrated into the dermis during development.

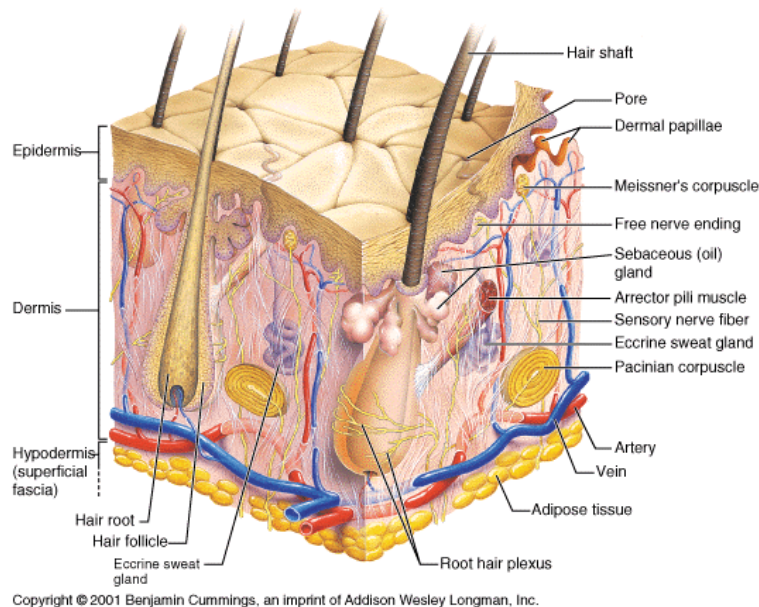


Figure 1.3: Structure of skin [8]

The epidermis, which is very thin, together with the rest of the epidermal system is removed during the unhairing and liming process. The lime and sulphide destroy the hair root and the inner epidermis.

Dermis or corium [6,7,9,10]: It consists primarily of dense connective tissue with stretch-resistant elastin fibres and supportive collagen fibres. Blood vessels, lymph vessels, and sensory receptors weave through the dermis. The fibre structure varies through the cross section of hide or skin. The fibres increase in size, reaching a maximum fibre diameter in the centre of the dermis and then decreasing a little as they approach to the next lower layer [9]. Leather is basically animal dermis that has been treated with chemical tanning agents. The differences between the leathers are largely due to variations in the fibrous structure. It may be fine and compact as in a calf skin, or rather loose and interspersed with fat cells as in the sheepskin.

An important feature of the dermis structure is the angle of weave. The magnitude of the angle can provide useful information regarding the process history of the pelt. The average angle of weave in raw skin is about 45 °; a lower value indicates greater depletion or relaxation of the dermis and a higher value indicates a degree of swelling [9].

Hypodermis or Flesh [6,9]: is the innermost layer of the raw skin and consist of loose convective tissue and adipose tissue (or body fat). Its purpose is to attach the skin to underlying bone and muscle and



connects the large blood vessel with the small ones running through the dermis. In addition, it serves as insulation for the body and stores energy in the form of lipids.

Flesh must be removed at the earliest stage possible in the processing programme (beamhouse operations, fleshing) because it creates a barrier that inhibits the penetration of chemical and biochemical processing reagents [9].

1.1.2 Collagen

Collagen is the principal structural protein accounting for approximately 30 % of all vertebrate body protein. The extracellular proteins of the main connective tissue consist of more than 90 % collagen in tendon and bone, and more than 50 % in the skin [11-13]. Because of the properties of collagen and its potential for chemical modification, this protein offers the tanner the opportunity to make a desirable product from an unappealing starting material [9].

Collagen comprises a family of genetically distinct molecules which have a unique triple-helix configuration of three polypeptide subunits known as α -chains in common [12]. So far, there are at least 28 types of collagen types described in literature which can be grouped into fibril-forming collagens, fibril associated collagens (FACIT), network-forming collagens, anchoring fibrils, transmembrane collagens and others, each type serving different functions in animals. Among them, fibril-forming collagen types I, II, III, V and XI are the most abundant collagen found in vertebrates [14-16]:

- **Type I** is the most widely occurring collagen in skin, tendon, bone, cornea, lung and the vasculature.
- **Type II** is limited essentially to cartilage.
- **Type III** found in relatively elastic tissues, such as embryonic skin, lung and blood vessels, and is found (5-10 %) in association with type I.
- **Type V** found as a quantitatively minor component in association with type I.
- **Type XI** found as a quantitatively minor component of cartilage in association with collagen II.

Since collagen type I is by far the most abundant protein found in the skin, therefore, here the term collagen will always refer to type I collagen unless otherwise specified.

Structure of Collagen

As mentioned earlier, the hallmark of a collagen is a molecule that is composed of three polypeptide chains, each of which contains one or more regions characterised by repeating amino acid sequence: Gly-X-Y, where Gly is glycine, and X and Y can be any amino, see Figure 1.4.

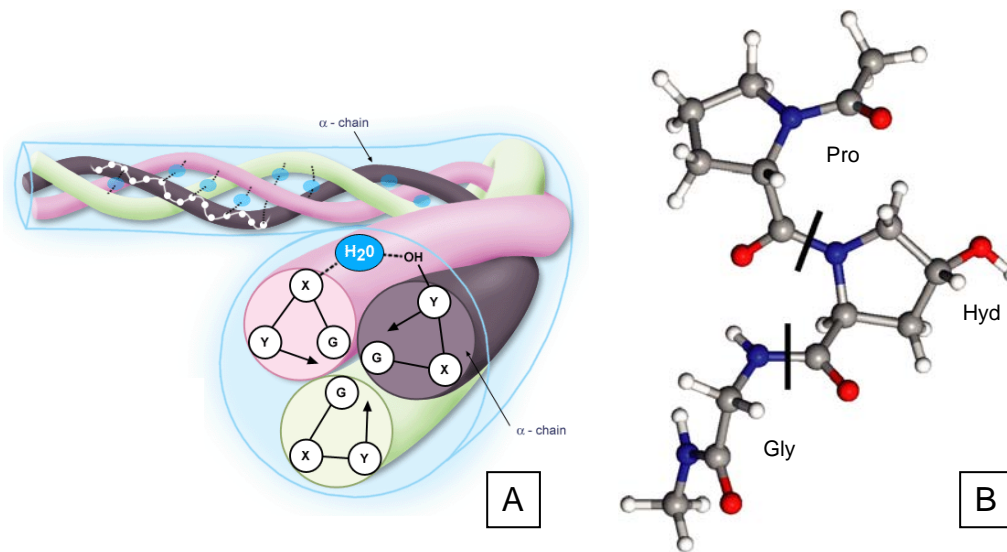


Figure 1.4: (A) Collagen Triple Helix [17]; (B) A view of the Pro-Hyp-Gly triplet [18]

Therefore, one third of the amino acids residues are glycine. Furthermore, X is often proline and Y is often hydroxyproline (Figure 1.4): 12% of triplets are (Gly-Pro-Hydro), 44% are (Gly-Pro-Y) or (Gly-X-Hydro) and 44 % are (Gly-X-Y), where X and Y are not defined. This sequence allows the chains to form a right-handed triple-helical structure, with all glycine residues positioned in the centre of the triple helix, while the side chains of the other amino acids X and Y occupy the outer position. In case of collagen Type I, the molecule is a heterotrimer with two identical α 1-chains and a third distinct α 2-chain.

In terms of leather it is the side chains that largely define its reactivity and its ability to be modified by stabilising reactions of tanning. However, the amino acid sequence plays only a minor role, see Table 1.1. The technologies for making leather are essentially the same for all animal skins and the variations in technologies are more dependent on the macrostructure and its age rather than the details of the chemistry of the protein [9].

Table 1.1: Amino acid contents for bovine skin. Residues per 100 residues [9]

Type	Aminoacids	Residues per 100
Non polar	Glycine	330
	Alanine	110
	Valine	22
	Leucine	26
	Isoleucine	12
Hydroxy	Serine	34
	Threonine	18
	Tyrosine	5
Carboxy	Aspartic acid + asparagine	47
	Glutamic acid + glutamine	73
Basic	Lysine	38
	Hydroxylysine	6
	Arginine	48
	Histidine	4
	Tryptophan	-
Imino	Proline	126
	Hydroxyproline	93
Sulfur	Cystine	-
	Methionine	4
Aromatic	Phenylalanine	14
	Tyrosine	5

The fibril-forming collagen molecules consist of an interrupted triple helix of about 300 nm in length (1000 amino acids) and 1.5 nm in diameter flanked by short non-helical telopeptides, which typically accounts for about 2 % of the molecule and are critical for fibril formation. The short non-helical telopeptides of the collagen monomers (tropocollagens) are involved in the covalent crosslinking of the collagen molecules as well as linking to other molecular structures of the surrounding matrix, see Figure 1.5.

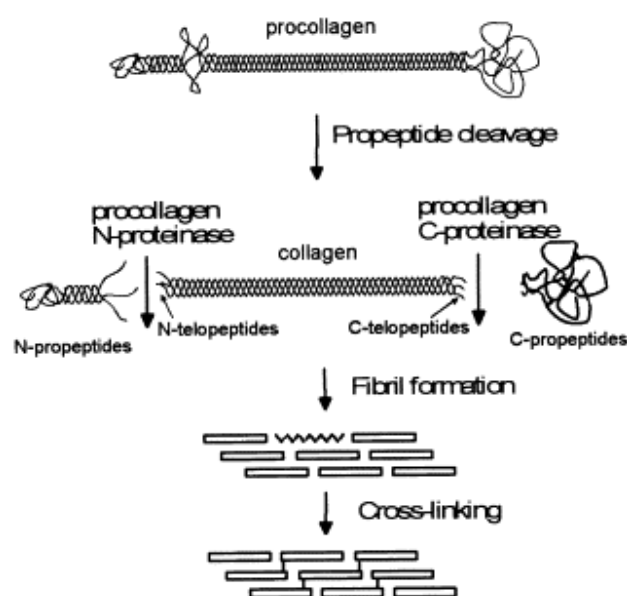


Figure 1.5: Schematic diagram to show the extracellular events involved in processing procollagen to collagen prior to fibril formation [19]

The mechanism of self-aggregation and crosslinking is described elsewhere [14]. However, in this process, the collagen molecules produce fine fibrils which are grouped together to form fibril bundles and these, in turn, are further grouped to create fibres as shown in Figure 1.6. The fibres characteristically divide and rejoin with other fibres throughout the corium structure. It is the variation in crosslinking or linking that provides the strength to the material [9]. In addition the degree of crosslinking increase with age and stress [12,20].

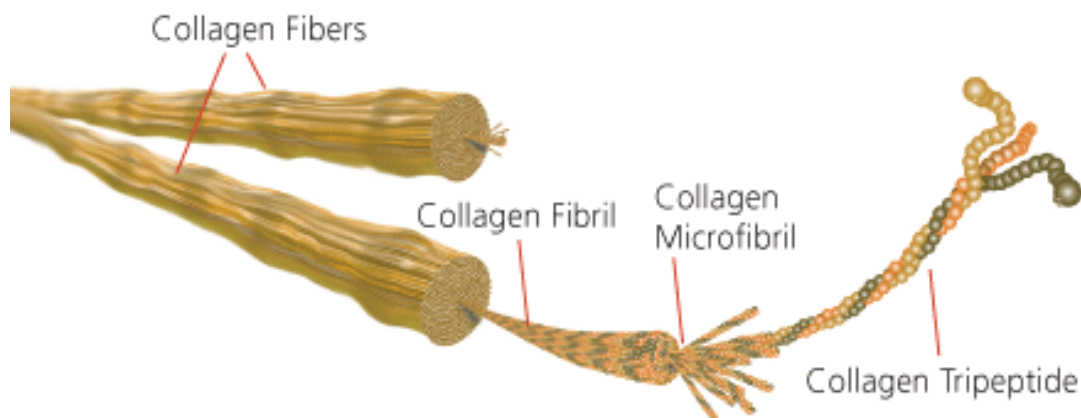


Figure 1.6: Hierarchical structure of collagen [21]

1.1.3 Tanning process

Tanning operations consist on transforming the raw skin that is a highly putrescible material into leather, a stable product, so that it can be used in the manufacture of a wide range of consumer products [22]. The tanning process can be divided into the following phases [5,6,9,23,24]:

- Preservation or curing process
- Beamhouse operations (preparation processes)
- Tanning process
- Post-tanning operations
- Finishing operations

Each phase involves one or more processing steps. Figure 1.7 illustrates these leather processing steps including the chemicals used and the waste produced.

Preservation (curing process)

Previous to the beamhouse operations, the animal hides or skins are dried or dehydrated with salts to prevent the animal hide and skins from bacterial decomposition. This pre-treatment is usually performed to allow for transport or storing without degradation of the skin or hide.

Beamhouse operations

The purpose of the beamhouse operations is to prepare the pelt for the tanning operations by purifying the pelt or "opening up" the pelt structure. In this sense, it consists basically in the removal of non-collagenous skin components and splitting the fibre structure at a level of fibril bundles, to separate them [9]:

- **Soaking:** This process enables the preserved raw dried hides to regain their water contents and open the contract fibres of the dried skins and remove undesired substances such as dirt, manure, blood, the denatured proteins, preservatives (sodium chloride, bactericides), etc. Upon soaking the skins become noticeable softer and cleaner which enables for further processing.

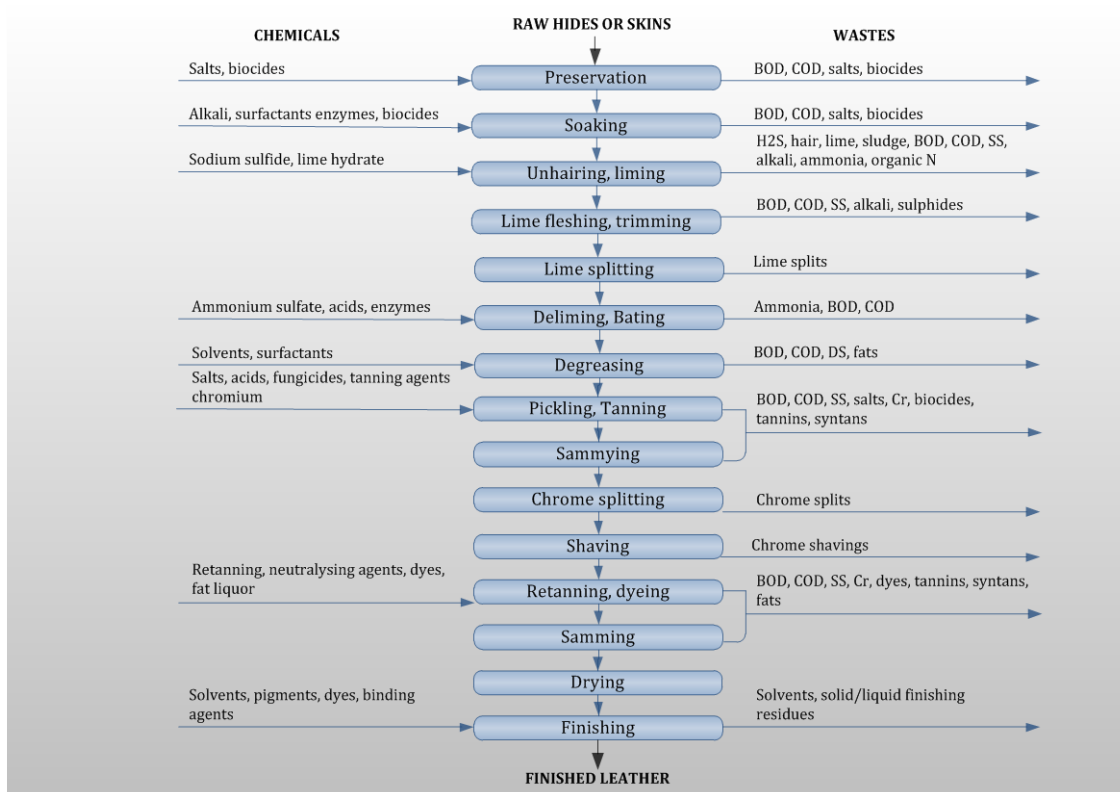


Figure 1.7: Leather processing steps [23]



- **Fleshing:** Is the mechanical removal of fat and connective tissue from the raw hide which otherwise would form a barrier that inhibits the penetration of chemical and biochemical processing reagents.

- **Unhairing / Liming:** Is the removal of extraneous tissue of epidermic matter including hair, interfibrillar proteins (albumins, globulins, etc.), degradation, and the elimination of mucoids and swelling of derm [23]. Lime and sodium sulphide or sulphhydrate are normally used to obtain this objective. Moreover, the liming process causes splitting the fibre structure at the level of fibril bundles which allow better penetration of reagents, for more effective reaction.

- **Deliming / Bating:** In the deliming process, the excess of lime and other chemicals are washed out from the hides. Later the alkaline hides are neutralized in a bath containing salts derived from a strong acid and a weak alkali (mainly ammonium salts) for the bating process. In addition, the lowering of the pH is accompanied by a significant degree of deswelling or depletion.

The bating process is an enzymatic digestion (proteolytic enzymes) that is used to remove non-structural proteins from the hides, hair and epidermal material from the grain and disarranges the collagen fibres in the hide.

- **Pickle:** Pickling is the acidification process of the hides by the addition of acid liquor (sulphuric, chloric, formic, and lactic) and salts (sodium chloride, sodium sulphate, and salts of the acid used) that enables the penetration of the tanning agents. The function of the acid is to protonate the carboxyl group because the chromium(III) tanning reaction only involves carboxylate groups.

- **Degreasing:** may be performed together with soaking, pickling, or after tanning to remove fats by leaching with organic solvents or surfactants. Fats may cause dyeing imperfections in the form of colourless acnes and the loss of physical strength. This operation is particularly important for sheepskins where the percentage of fat substances on raw weight is about 30-40 % [23].

Tanning

It is the process in which the raw hides and skins, a putrescible material, are converted into leather, a stable material, which is resistant to bacteria attack and has enhanced resistance to wet heat (hydrothermal stability). The most important tanning processes are: chromium tanning and vegetable tanning. However, chromium(III) tanning is used by most of the leather industry (90 %), mainly due to the



short time (4-6 hours), low cost and because it produces leather that it combines both the best chemical and physical properties sought after in the majority of leather uses [24-26]. Chemically it is based on the crosslinkage of chromium(III) ions with free carboxyl groups in the collagen [9]. At this stage, the product from the chromium(III)-tanned is named wet-blue for its colour derived from the chromium.

Post-tanning operations

- **Wringing (Sammying):** Removal of excess of moisture from the stock for a proper splitting.

- **Splitting:** Adjust of the thickness to the requirements for the end use.

- **Retanning:** Further tanning agents are used to modify the properties according to the end user. These changes include the handle, the chemical and hydrothermal stability or the appearance of the leather.

- **Dying (colouring):** Is the process to give the required colour of the leather. Applying dye in solution or pigment, to confer dense, opaque colour, can be performed in the drum or colouring agents may be sprayed or spread by hand (padding) onto the surface of the leather [9].

- **Fatliquoring:** it prevents fibre sticking during the drying by providing an oil surface to the fibre structure, which then gives it the required lubrication. A secondary effect is to control the degree of softness conferred to the leather.

Fatliquoring is usually conducted with self-emulsifying, partially sulphated or sulphonated (sulphited) oils, which might be animal, vegetable, mineral or synthetic. This step may also include processing to confer the leather a required degree of water resistance [9].

- **Setting out:** the objective is to smooth the grain as well as to remove excess of moisture.

- **Drying:** The leather is dried to certain moisture level. In addition, it also contributes to the chemical reactions of the leather-making.

Finishing Processes

It comprises a number of operations to fulfil the final product specifications.

1.1.4 Tannery waste

The tannery industry generates large amounts of solid wastes, and especially, of wastewater containing different loads of pollutants, as well as produces air emissions to the environment.

1.1.4.1 Waste effluents

1.1.4.1.1 Characterisation of wastewater

Effluents from the rawhide processing tanneries, which produce wet-blue, contain compounds of trivalent chromium and sulphides in most of the cases [23]. However, the environmental impact not only concerns the load and concentration of the classical pollutants, but also the use of certain chemicals such as biocides, which are used in tanneries to control the growth of various forms of life on leather, and surfactants and organic solvents, which are responsible for the high BOD (biological oxygen demand) and COD (chemical oxygen demand) values and represent a huge pollution load. This high load and pollution problem in the effluents, together with suspended solids, results in a high cost in concern with the effluent treatment in leather production.

The pollution load changes in function of the leather processing step and type of raw hide or skin. Table 1.2 shows the pollution load generated in each processing step for bovine salted raw hide. Values for other types of raw hides or skins can be found elsewhere [27].

Table 1.2: Pollution values from tannery processes under conditions of good practice (2008). Values per tonne of bovine salted raw hide [27]

	Beamhouse	Tanning	Post tanning	Finishing	Total
Water (m ³ ·t ⁻¹)	7 - 25	1 - 3	4 - 8	0 - 1	12 - 37
COD (kg·t ⁻¹)	120 - 160	10 - 20	15 - 40	0 - 10	145 - 230
BOD ₅ (kg·t ⁻¹)	40 - 60	3 - 7	5 - 15	0 - 4	48 - 86
SS (kg·t ⁻¹)	70 - 120	5 - 10	10 - 20	0 - 5	85 - 155
Cr ³⁺ (kg·t ⁻¹)	-	2 - 3	1 - 2	-	3 - 7
S ²⁻ (kg·t ⁻¹)	2 - 9	-	-	-	2 - 9
TKN (kg·t ⁻¹)	9 - 14	0 - 1	1 - 2	-	10 - 17
Cl ⁻ (kg·t ⁻¹)	120 - 150	20 - 60	5 - 10	-	145 - 220
SO ₄ ²⁻ (kg·t ⁻¹)	5 - 20	30 - 50	10 - 40	-	45 - 110
Grease (kg·t ⁻¹)	5 - 8	1 - 2	3 - 8	-	9 - 18
TDS (kg·t ⁻¹)	200 - 300	60 - 120	40 - 100	-	300 - 500



1.1.4.1.2 Conventional Treatment

The following treatment steps are typically used in contemporary tanneries, which include three main steps of the treatment, e.g., mechanical treatment, physico-chemical treatment, and post-purification, sedimentation and sludge handling.

Mechanical treatment

It is usually the first treatment of the raw effluent that includes screening to remove coarse material. Up to 30-40 % of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils and gravity settling [3,23].

Physico-chemical treatment:

After the mechanical treatment, the physico-chemical treatment is usually carried out, which involve the chromium(III) precipitation and sulphide treatment. Coagulation and flocculation are also part of this treatment to remove a substantial percentage of the COD and suspended solids [3].

- **Chrome precipitation:** The trivalent chromium-containing effluents is precipitated with alkalis such as sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), calcium hydroxide ($\text{Ca}(\text{OH})_2$) and magnesium oxide (MgO). The difference between them is the effect they have on the precipitate: the faster the basifying reaction, which is dependent on the alkalinity and the solubility, the more voluminous is the precipitate and the slower is the settling rate. Therefore, the greatest sludge density is obtained using magnesium oxide. The addition of polyelectrolyte can improve flocculation [28].

After settling and dewatering of the chromium(III) oxide suspension, the filter cake is re-dissolved in sulphuric acid, to control the desired causticity of the product. In order to ensure complete solubilisation of the chromium(III) sludge, the reaction should be carried out at above 70 °C [28]. The basic chromium(III) sulphate solution can be re-used for tanning by recycling into the tanning process and by re-placing 20-35 % of the "fresh" added chromium(III) tanning salt [3,23]. By means of this method it is possible to obtain an effluent with less than 10 $\text{mg}\cdot\text{l}^{-1}$ of chromium (III) expressed in Cr, see Table 1.3.

From a chemical point of view, chromium(III) recycling is a simple process with excellent environmental results however, it requires careful analytical control and special equipment [3,28].

- **Sulphide treatment:** Commonly sulphide-containing effluents from beamhouse operations are treated separately and at pH above 9 because at a lower pH the formation of toxic hydrogen sulphide gas can occur. The sulphides from delimiting and pickling liquors can be easily oxidized in the drum by adding hydrogen peroxide (H_2O_2), sodium metabisulphite ($Na_2S_2O_5$) or sodium bisulphite ($NaHSO_3$). Where the segregation of sulphide-bearing liquors is not possible, the sulphides are generally removed by means of precipitation with iron (II) salts and aeration. However, a disadvantage of this method is that generates high volumes of sludge [3].

The effluent after the mechanical and physico-chemical treatments is generally easily biodegradable in standard aerobic biological treatment plants [3]. Table 1.3 shows the typical performance for tannery waste water treatment.

Table 1.3: Typical performance for tannery waste water conventional treatment [29]

Parameters	COD		BOD ₅		SS		Cr ³⁺		S ²⁻		TKN	
	%	mg·l ⁻¹	%	mg·l ⁻¹	%	mg·l ⁻¹	%	mg·l ⁻¹	%	mg·l ⁻¹	%	mg·l ⁻¹
Pre-treatment												
Grease removal (dissolved air flotation)	20-40											
Sulphide oxidation (liming and rinsing liquors)	10								10			
Chromium precipitation							2-10					
Primary treatment												
Mixing + Sedimentation	25-35		25-35		50-70		20-30				25-35	
Mixing + Chemical treatment + Sedimentation	50-65		50-65		80-90		2-5		2-10		40-50	
Mixing + Chemical treatment + Flotation	55-75		55-75		80-95		2-5		2-5		40-50	
Biological treatment												
Primary or chemical + Extended aeration	85-95	200-400	90-97	20-60	90-98	20-50	<1		<1	50	150	
Primary or chemical + Extended aeration with nitrification and denitrification	85-95	200-400	90-97	20-60	90-98	20-50	<1		<1	80-90	30-60	

Post-purification- sedimentation and sludge handling

These are the last step in waste water treatment. With sedimentation the sludge in the waste water treatment plant is separated from the water phase by gravity settlement. After dewatering this sludge by

means of filter presses, a sludge cake with up to 40 % dry solids can be achieved, whereas belt presses produce a sludge cake with up to 20 – 25 % dry solids. Centrifuges achieve up to 25 – 45 % dry solids and thermal treatment up to 90 % dry solids. Energy is an important factor in these processes [3].

Limits on the total chromium(III) discharge effluent vary widely between 0.05 and 10 mg·l⁻¹ for direct discharges into standard water bodies and 1-50 mg·l⁻¹ on indirect discharges into sewage systems. The WHO standard for the acceptable amount of chromium(III) in drinking water is 0.05 mg·l⁻¹ [23].

1.1.4.2 Solid wastes

1.1.4.2.1 Characterisation of solid waste

Large amounts of solid waste are generated during the manufacturing of leather. Figure 1.8 shows the amounts of solid waste generated in different leather processing steps for bovine salted hides.



Figure 1.8: Amount of solid waste generated during the manufacturing of leather for bovine salted hides per tonne of raw hide treated



1.1.4.2.2 Conventional treatment

The way to treat the solid waste from the leather industry differs between untanned solid waste and chromium(III)-tanned solid waste. Traditionally, untanned solid waste has been recycled because their recovery is profitable (gelatine). There are several options for recycling or re-using which includes, but are not limited to the following:

- As raw material for glue, gelatine or food casing production.
- Tallow recovery from raw trimmings, fleshing and splits, which is performed in rendering plants. Limed trimmings, fleshing and splits may need pre-treatment before conversion.
- Recovering of hair: keratin hydrolysate for cosmetics and pharmaceutical products; or for conversion into fertilizer.

Unlike untanned solid waste, land application and disposal of chromium(III)-tanned solid waste has been widely practiced during most of the twentieth century, and only in minor cases it have been recycled for leather fibreboard production. On the other hand, sludge from wastewater treatment has been further treated for composting, recycling in agriculture, anaerobic digestion, landfill and thermal treatment. In any case, regardless of the method, the safe disposal depends on the chromium(III) content. Although, chromium(III)-tanning is based on chromium(III) which is not toxic, the possibility of Chromium(III) being converted to Cr (VI) by oxidation under some specific conditions of alkalinity ($\text{pH} > 9$), temperature and aeration of the soils [30-33] exists and it should be taken into consideration [34,35]. Nevertheless, there is no evidence of leaching of chromium(III) in any form from the solid waste under normal conditions, and even under experimental conditions combining maximum aeration and high pH, the chromium(III) is not oxidized to chromium(VI) in soil [36-39].

Disposal of this solid waste is rather expensive and environmentally inappropriate way of handling a waste material that has the potential for reutilization [4] due to the collagen content. In addition, this option is likely to become more restricted and this waste may require pre-treatment before disposal. It will also require more extensive definition in terms of chemical content and behaviour in the landfill environment, because leachability and ecotoxicity are not completely known [22].

Therefore, over the last years several studies have been carried out to find feasible ways of treating the chromium(III)-tanned solid waste and sludge [40-56]. Those methods are mainly based on chemical and/or enzymatic hydrolysis [57-63] with or without a previous dechroming, when the objective is to



remove as much chromium(III) from the chromium(III)-shavings as possible, so both chromium(III) and collagen products can be reused. Those treatments aim to enhance the reusability of this kind of waste [35].

1.1.5 Gelatine / By-product from tannery industry

Degradation of collagen by partial hydrolysis (wet heat conditions) causes the transition of the triple helix to a random coil which is known as gelatine [9]. Gelatine is a nutritious protein containing amino acids [64] which a worldwide production of 300,000 tonnes per annum.

1.1.5.1 Manufacture

In the production of gelatine, the collagen is extracted from skin, connective tissue and bones of animals. The most abundant sources of gelatine are pig skin (46 %), bovine hide (29.4 %) and, pork and cattle bones (23.1 %). The main steps in the manufacturing process are washing, pre-treatment, extraction, purification and recovery or concentration [64-66].

Washing

The raw material is initially washed to remove the impurities. This step also includes degreasing and demineralization of bone to produce ossein [64].

Pre-treatment or conditioning

The collagen contained in animal connective tissue dissolves very slowly, even in boiling water. This is because of the crosslinked nature of collagen [65]. Thus prior to extraction, gentle chemical treatment is necessary to break down a sufficient number of crosslinks and enable the release of free α -chain [64,65]. In addition, the process is also designed to remove other natural organic substances such as proteoglycan, blood, mucins, and sugars.

The process conditions in the pre-treatment process as well as in the extraction process are chosen accurately by the manufacturer in order to obtain gelatine with the desired physico-chemical properties. The type and degree of crosslinking is dependent on the age of the animal. For older animals, more intense alkaline treatment is preferred, while for younger ones a short period of conditioning with very



dilute acid is all that is necessary [65]. Moreover, the gelatine obtained from acid treated raw material is commercially known as type A gelatine (isoelectric point at pH ~ 8 - 9), whereas the gelatine obtained from alkali treated raw material is referred to as type B gelatine (isoelectric point at pH ~ 4 - 5).

Extraction

The material is then processed in a multi-stage process under neutral or acid conditions at different temperatures. The extraction process is designed to obtain the maximum yield by optimizing the balance between pH, temperature and extraction time [64]. In practice gelatine is obtained from the raw material in three or four separated extractions, each at an increasing temperature from 50 °C to about 100 °C.

Purification

The dilute gelatine liquor is then filtered to remove the suspended collagen particles, fat globules and foreign proteins. The gelatine is further purified by deionization which both removes inorganic salts left from the pre-treatment and also adjusts the pH to that suitable for sale (pH \cong 5.0 to 5.8) [64].

Concentration

The final stage is evaporation, sterilization, and chilling and drying. Because gelatine is susceptible to thermal hydrolysis it is necessary to keep the evaporation time and temperature to a minimum and therefore vacuum is applied [65]. Subsequent to final sterilization, the gelatine solution is chilled and air-dried until the final moisture content is in the range of 8-13 %. Lower moisture contents than this can cause poor dissolution or even partial insolubility of the gelatine [66].

1.1.5.2 Structure and composition

Gelatine contains a total of 18 amino acids, including nine essential amino acids (AA), which are joined together in sequences to form polypeptide chains of 1000 amino acids. The composition of gelatine is variable depending on raw material and process used, but the average amino acid distribution for the three α -chains found in gelatines Type A and Type B is shown in Table 1.4.

Table 1.4: Amino acid composition of gelatine, residues per 1000 residues [65]

Aminoacids	Type A	Type B
Alanine	112	117
Arginine	49	48
Aspartic acid + asparagine ⁽¹⁾	45	46
Cystine	-	-
Glutamic acid + glutamine ⁽²⁾	73	72
Glycine	330	335
Histidine ⁽³⁾	4	4.2
Hydroxylysine	6.4	4.3
Hydroxyproline	91	93
Isoleucine ⁽³⁾	10	11
Leucine ⁽³⁾	24	24.3
Lysine ⁽³⁾	27	28
Methionine ⁽³⁾	3.6	3.9
Phenylalanine	14	14
Proline	132	124
Serine	35	33
Threonine ⁽³⁾	18	18
Tryptophan	-	-
Tyrosine ⁽³⁾	2.6	1.2
Valine ⁽³⁾	26	22
⁽¹⁾	Type A: Aspartic acid 29, asparagine; Type B: Aspartic acid 46	
⁽²⁾	Type A: Glutamic acid 48, glutamine 25; Type B: Glutamic acid 72	
⁽³⁾	Essential amino acids	

The only additive sometimes incorporated during the manufacturing is sulphur dioxide as colour inhibitor during the extraction and evaporation and not as a preservative. There is also a small proportion of carbohydrates (1-1.5%) in the form of glucose and galactose bound to gelatine at hydroxylysine residues [64].

1.1.5.3 Gelatine properties

Gelatine is a vitreous, brittle solid that is pale yellow to white and nearly tasteless and odourless. The multi-functional properties of gelatine can be divided into two groups. The first has properties associated with gelling and the second group relates to surface behaviour of gelatine [65]:

Properties associated with gelling

Solubility: Gelatine is partially soluble in cold water, it can swell and absorb up to 10 times its weight in water, but can be dissolved by stirring in hot water. The rate of solubility is dependent on the temperature, concentration and particle size. Gelatine is insoluble in alcohol and most other organic solvents [64].



Amphoteric behaviour: The isoelectric point (IEP) is defined as the pH at which no net migration takes place in an electric field, while the isoionic point is defined as the pH at which there is no net charge on the molecule. In a deionized solution, the isoelectric and isoionic points are for most purposes identical [64].

The IEP of gelatine is dependent on the type of pre-treatment applied during manufacture. For gelatine of type A, this corresponds to collagen at about pH 8–9 and for type B at pH 4.8–5.5. At pH levels lower than the IEP, the molecule will have a net positive charge, and above this point a net negative charge.

For practical purposes, it is important to know that turbidity, firmness and compatibility of gelatine with other hydrocolloids can be affected by the IEP and pH of gelatine [35,65].

Gel formation: The most important technological property of gelatine is its thermally reversible gelling properties. Gelatine is a mixture of polymer chains of different lengths. Thus, after dispersion and swelling on cold water, it gives on heating a colloidal solution or sol which on cooling forms a gel. The gel formation, viscosity and texture are determined by the structure, molecular size and temperature of the system [65].

An important element determining the quality of gelatine is the firmness or strength of the gel set, which gives an indication of the level of hydrolysis that can be achieved as it is related to the level of degradation of the collagen fibres [67]. Having a low gel strength indicates that the degradation of the collagen fibres is high. The gel strength is nearly always quoted as Bloom strength [35,62,68]. The Bloom value is expressed as the mass in grams necessary to produce the force which, applied to a plunger 12.7 mm in diameter, makes a depression 4 mm deep in a gel having a concentration of 6.67 % by wt. and matured at 10 °C [64].

In industrial practice, however, there are other factors affecting the properties of the gelatine. The gelatine/water system depend strongly on the type of gelatine or manufacturing conditions, the thermal and mechanical “history”, the ratio of water to gelatine, the presence of other ingredients and a number of other parameters [64].

Surface effects:

The surface properties of gelatine are based on the fact that the gelatine side chains, like those of all proteins, have charged groups and that certain parts of the collagen sequence contain either hydrophilic or hydrophobic amino acids [65].



Emulsifying properties: gelatine promotes the formation and stabilization of an emulsion, and is used, for instance, in the manufacture of toffees and water in oil emulsions such as low fat.

Foaming properties: gelatine is an efficient foam stabiliser. In the production of aerated confectionary products such as marshmallows, gelatine is able to produce and support foam and to produce a rapid setting at the air/liquid interface by forming a film around entrapped air bubble.

Film forming properties: Gelatine has excellent film-forming and good mechanical properties. In addition, it is unique among hydrocolloids in forming thermo-reversible films. Film forming properties are used in the manufacture of hard and soft pharmaceutical capsules and casing applications.

Protective colloid properties: Gelatine is a very effective protective colloid. It prevents the aggregation of crystals and particles and hence stabilizes heterogeneous suspensions and dispersions. In the case of photographic emulsions as coated onto photographic carrier material such as film or paper, gelatine acts not only as a carrier and binding agent for the light-sensitive coating, it also functions as a protective colloid. The same function is also utilized in the ice cream industry; here the addition of gelatine enhances the formation of very fine crystals, thus preventing coarse crystallization of the lactose in the mixture [65].

Adhesion properties: For instance, cereal bars with low water contents are produced by adding gelatine hydrolysate as a binding agent.

1.1.5.4 Applications of gelatine

About 70 % of the gelatine produced is used in the food industry and about 15 % in the pharmaceutical industry [66], while the remaining being used in other applications such as photographic, cosmetics, medical, etc.

Food Industry

Gelatine is widely used as an ingredient in the food industry, due to the following functional properties [64]:

- It forms high-quality gels in dilute solution with typical clean, melt-in-the-mouth textures.
- It forms elastic gum-type textures in the concentrated gel, slowly dissolving in the mouth.
- It forms stable gels on cold storage.

- It produces emulsification and stabilization of immiscible liquid/liquid, liquid/air or liquid/solid mixtures.
- It acts as a polyelectrolyte to flocculate suspended particles or unstable colloids from dilute solutions.
- It acts as a water retainer (it swells easily and there is no syneresis).
- It acts as an efficient tableting aid and binder.

Gelatine is sold in many sections of the food industry including, but are not limited to the following: in table jellies, confectionary, meat products, ice-creams, low-fats and very low-fats spreads, and chilled dairy products.

Pharmaceutical industry

In the pharmaceutical industry about 80 % of the gelatine is used predominantly in the manufacture of hard and soft capsules, the remaining being used for microencapsulation, tablet binding, tablet coating, emulsion stabilization [66].

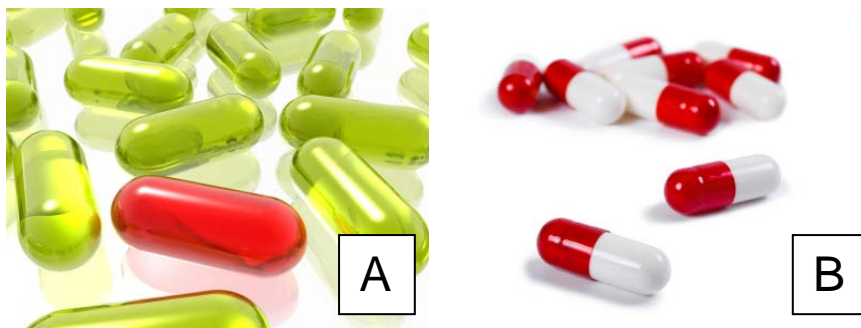


Figure 1.9: Soft (A) and hard (B) gelatine capsules [69]

Photographic industry

Photographic industry exploits the unique combination of gel formation and surface activity to suspend particles of silver chloride or light-sensitive dyes, without any agglomeration [64].

Other Technical applications [35]

- Used as a carrier, coating or separating agent for other substances.
- Additive in washing up liquids, protecting skin and delicate textiles against the aggressive surfactants.
- Gelatine is closely related to bone glue and is used as a binder in match heads and sandpaper.



- Cosmetics may contain a non-gelling variant of gelatine under the name "hydrolysed collagen".
- As a surface sizing, it smoothes glossy printing papers or playing cards and maintains the wrinkles in crepe paper.
- Book restoration.
- Blocks of ballistic gelatine simulate muscle tissue as a standardised medium for testing firearms ammunition.
- Gelatine and collagen hydrolysates are used as fertilisers, thanks to the slow depletion of amino acids, the nitrogen is dosed.
- Cleaning of zinc and cadmium in electrolytic baths; gelatine enables the sedimentation of dirt.
- Gelatine is used as an elastic adhesive in the restoration of buildings.
- Gelatine is used by synchronised swimmers to hold their hair in place during their routines as it will not dissolve in the cold water of the pool.
- It is commonly used as a biological substrate to culture adherent cells.
- Fighting oil disasters (in development): the addition of gelatine would transform the oil suspension into a jelly phase, solidifying the oil spillage and being able to cut and store it.

1.1.6 Novel treatment process (recovery, re-use)

Chromium(III) tanned waste cannot undergo traditional process for obtaining gelatine or industrial glues due to chromium(III) presence that performs the skin structure stabilization. Therefore, recovery of collagen from chromium(III) tanned wastes requires removal of the chromium(III) present in the tanned wastes (dechroming process) without affecting the collagen structure and avoiding the thermally labile regions.

So far, three dechroming processes, which have been studied for more than half a century, are described with acids, alkalis and complexing agents; the treatment with reducer and/or oxidizer agents [70], and treatments with enzymes [71,72]. From all those, the oxidation reaction of chrome (III) to chrome (VI) through the use of hydrogen peroxide in an alkaline medium is one of the best procedures.

The method was proposed in 1975 by Cot and Gratacós [70] and further developed by Vera et al.[73], Cot and Granell [44,45,74-78] and Cot et al. [46,79,80]. Since 1992, the research group formed by Ecotechnology division of IQS (Institut Químic de Sarrià) and Ecotechnologies department (CID-CSIC of Barcelona) followed the studies on this research line [81-85].



The advantages of this method lie in the fact of a high-speed oxidation reaction (around 1 hour) and that the collagen fibres are left with a very little residual chromium(III) and, with their physical and chemical characteristics completely unaffected. In this way, it is possible to isolate a high added value of collagenic biopolymers, which in turn, can be used for a wide range of potential applications in the fields of leather, textile, paper, wood and, even might be in the fields of pharmacology, cosmetics, veterinary science, and medicine. Moreover, the effectiveness of the current method for chrome removal suggests that it is possible to set up an alternative process to recover chrome (III) from tannery effluents [46,78,84].

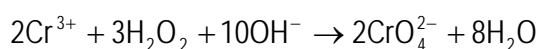
In general, the developed dechroming process lies in the following stages:

Grinding process:

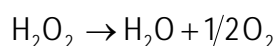
Ground up collagenic chrome (III) wastes into a defibered size, fixed into: a diameter of 1 to 5 mm; so giving a more homogeneous material with a greater surface and therefore saving chemicals and shorten reaction time.

Dechroming process:

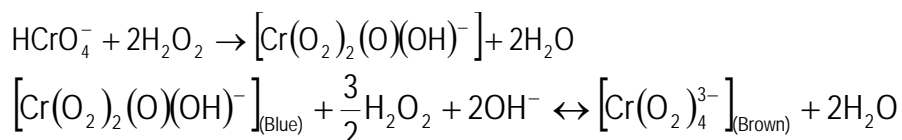
The oxidation takes place in basic medium; therefore, a pH 12 should be reached using, sodium carbonate or sodium hydroxide and the oxidation is carried out with hydrogen peroxide that allows a faster kinetic reaction and in addition does not generate any residues. This reaction only forms water as show the following reaction [26,86].



The compound acting as oxidizing agent is oxygen that comes from hydrogen peroxide decomposition



During this phase, a brown precipitate is observed, that can be identified as peroxochromates of hard isolation. The reactions are presented in the following equations:



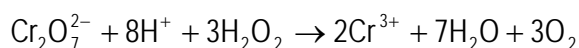


The blue complex is present in neutral medium and the brown complex in an alkaline medium. This is favored by hydrogen peroxide excess and the basicity of the sample. This reaction is influenced by the oxygen diffusion in reaction medium.

Centrifuge operation:

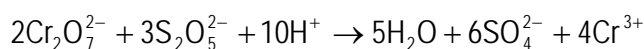
This operation produces a filtrate (liquid effluent) and a dechromed collagenic fibres (solid state). The filtrate, which contains chromium(VI) is stored into a stainless steel stirred tank for further reduction to chromium(III), and adjusted to the correspondent basicity (33° Sch); then this basic chromium(III) solution can be mixed up with the addition of chromium(III) salts powder to the right concentration for the tanning operation. The main reducing agents are the following:

➤ **Reduction with hydrogen peroxide:**



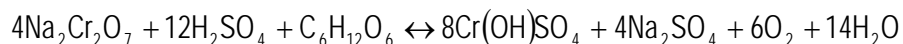
for acidic medium.

- **Reduction with sodium disulphite:** The method of obtaining chromium(III) liquor with disulphite is very similar to the one using the sulphite. In this case, disulphite reacts with acid forming sulphite that acts as reducer and yields bigger quantities of sulphates. Next equation shows the global reaction that governs the process.



This reduction generates an important amount of complex and neutral salts. In addition, the reaction could be developed in cold and also without using sulfuric acid.

- **Reduction with glucose:** This is one of the most widely used reduction methods to apply in chromium(III) recovery process. In this reaction, glucose is not completely oxidized to carbon dioxide, but some intermediate compounds are formed, generally organic acids that play an interesting role because of their influence diminishing the basicity and masked effect on chromium. The following equation shows the reaction when the glucose suffers a complete oxidation.



The masked effect increases as the quantity of glucose is increased favoring the formation of organic acids. On the contrary, the temperature reduction produces a diminishing effect upon the basicity. One problem that arises when using this method is the doubts about if it is much better adding glucose to the acid-dichromate mix or adding acid to the glucose-dichromate mix. Alternatively, the squeezed dechromed collagenic fibers are driven through a conventional pump into the next step.

Isolation of collagen biopolymers

Treated dechromed collagen wastes undergo a second process of highly controlled topochemical hydrolysis. The method of control depends on the degree of interaction of the following variables

- **Macerators:** alkaline, acid , liotropic.
- **Activators:** peroxides – hydrogen peroxide, sodium percarbonate, sodium perborate, etc.

It is important to stress that during the process, a certain amount of peroxochromates are generated *in situ*, which in turn are very active and possess a high oxidation capacity. These compounds contain 2, 5 peroxy groups for each chromium atom, and are strongly linked to the ionic groups of the collagen structure. The presence of such peroxochromates during the second hydrolytic process, carried out at a temperature of - 60 °C - 70°C, accelerates the kinetics of the reaction, allowing the production of the bioproducts such as gelatine with acceptable physical and mechanical properties. After two hours a yield of 98% or higher was reached [80,84,85,87].

Storage

These biopolymers can be stored either in a completely dry state or in a solution of 30% concentration.

1.1.7 References

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1.2 Thermal energy storage: built environment

The increased demand for energy, the rise in the price of fuel associated with the depletion of fossil fuels, and the growth of CO₂ emissions all require the development of more energy-efficient processes and a shift from non-renewable energy sources to renewable energy sources. In this sense, thermal energy storage and conversion (TESC) aims to improve the thermal efficiency of a process by harnessing waste heat from industrial process, power plants, combustion engines, or even from renewable energies.

Heat is the form of energy most widely used in industry and power plants for driving the processes or producing electricity, either through steam or in fired furnaces. Also, in internal combustion engines, heat is used for driving vehicles or other equipment through the combustion of fuel. As a consequence of the work produced, most of this heat is degraded to a lower level and is released to the environment through cooling water, cooling towers, flue gases or other means. This waste heat is left unused due to its relatively low grade. It should be borne in mind that, for instance, the average global efficiency of fossil-fuelled power generation is generally between 35 to 45 % [1], and the energy conversion efficiency from fuel to driving work in vehicles is around 20 % [2].

Thermal energy storage and conversion allows storing, transporting and re-using this waste heat or even converting this waste heat for heating and cooling application by changing the quality of heat supplied and the heat required. Moreover, considering that in 2004 the heating and cooling demands of the industrial, commercial and domestic sector accounted for between 40-50 % of the total global 320 EJ (7,639 Mtoe) final energy demand [3], TES could contribute to substantial energy savings and a reduction in CO₂ emissions [4].

In addition to the aforementioned applications, perhaps the most important applications for thermal energy storage and conversion are with solar energy, as well as other renewable thermal energies. TESC may contribute to bridge the gap between energy supply and energy demand that are due to seasonal and daily changes. This is between seasons, between day-time and night-time or even between sunny and cloudy days. Therefore, TESC would contribute to increase the potential of solar energy for its further and quicker implementation, reducing fossil-fuel consumption and thus contributing to significantly reduce the greenhouse effect.

One potential application of solar thermal energy storage is on households. In 2005, the energy consumption in households was 82 EJ (4.5 Gt of CO₂ emissions) of which 69 % is for space heating and

domestic hot water. This energy consumption can be reduced by applying energy saving measures [5-8] such as improved insulation, heat recovery ventilation, etc. (low energy buildings), while the remaining energy demand could be covered by solar energy. However, in winter period, there is a deficit of solar energy respect to the energy demand, see Figure 1.10. By contrast, in summer period, there is an excess of solar energy versus demand, which could then be stored to fulfil the energy demand in winter period.

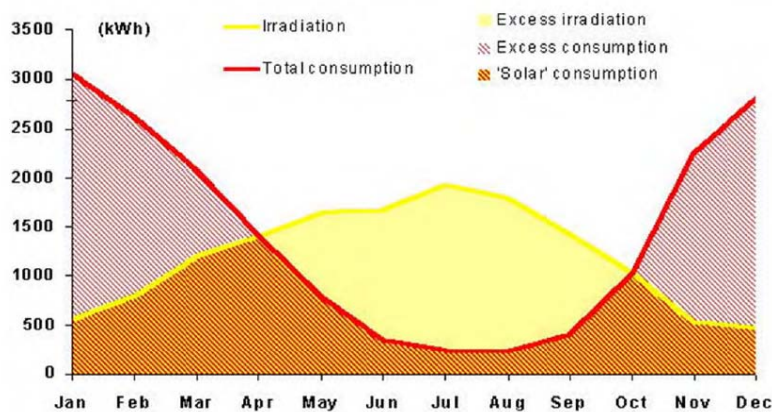


Figure 1.10: Annual energy demand – Excess of solar heat in summer months, deficit in winter months [9]

Hadorn [5] estimated that the heat storage required to fulfil the demand for space heating and domestic hot water during the winter period without available solar energy was about 1850 kWh (6.7 GJ), for a low energy building. Now the question arises, how to store (and deliver) the heat collected during the summer that is not only technically feasible but also economically viable for a low energy single family houses?

1.2.1 Types of Thermal Energy Storage

Thermal energy can be stored by sensible heat, by latent heat, by sorption process or by chemical reaction.

1.2.1.1 Sensible Heat

1.2.1.1.1 Description

In sensible heat storage, heat is stored by increasing the temperature of the material such as water, air, oil, rock, sand, bricks, soil or molten salts [10]. The energy storage density is related to the product of the specific heat of the material and the temperature change.

1.2.1.1.2 Applications

The research on solar thermal energy storage by sensible heat is mainly focused in the built environment and in solar power plants.

Built environment

Traditionally, water is used in households for storing solar heat for short periods of time. However, for a longer period (seasonal heat storage), the storage tank is too large to be placed inside a single family house. A roughly estimation of this volume for a low-energy house in mid-Europe, would require a water tank of 34 m³ to meet the heating demand in the winter period, including heat losses [11], see Figure 1.11. Therefore, this type of storage technique can then only be economical if applied on a large scale (> 100 houses) [10,12].

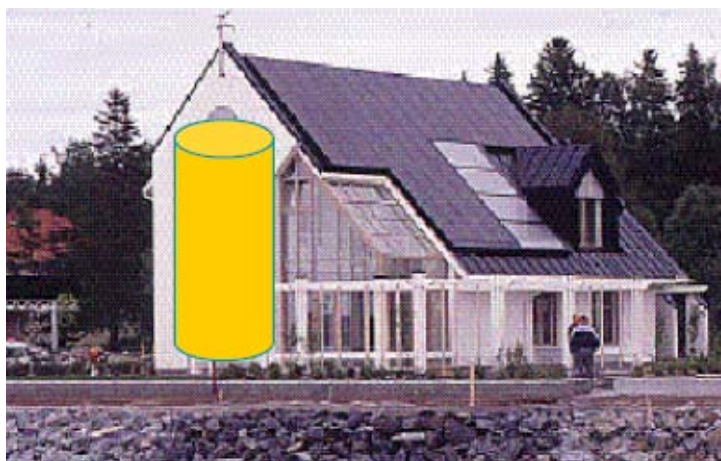


Figure 1.11: Hypothetical size of storage tank for low-energy house [11]

There are four main technologies for large-scale seasonal thermal storage, that have been developed, tested and monitored over recent decades [13] see Figure 1.12. Background information on those technologies as well as the existing demonstration plants can be found elsewhere [10,13-16]; however, a brief description is given now.

The decision to use a certain technology mainly depends on the local conditions and, primarily, on the geological and hydro-geological situation in the ground below the respective construction site [14].

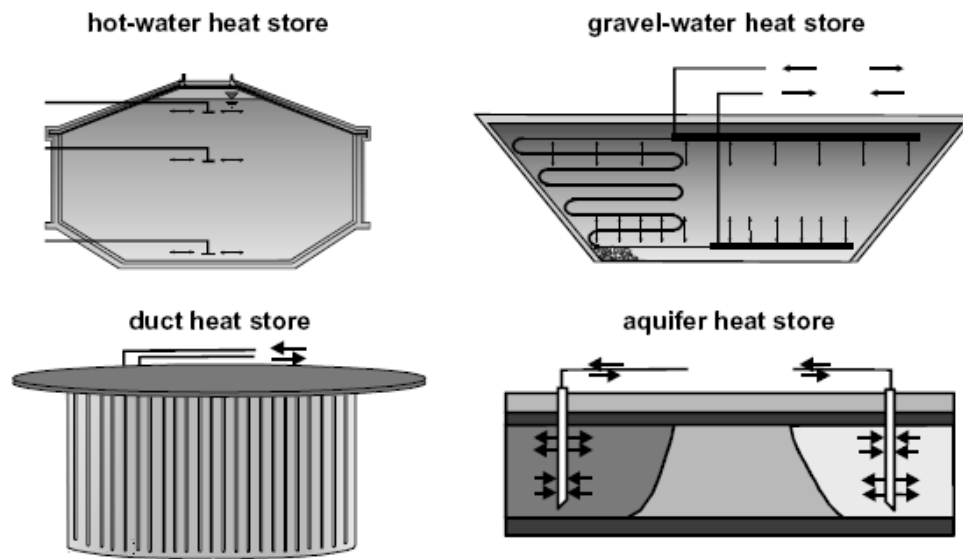


Figure 1.12: Four main technologies for seasonal heat storage by means of sensible heat [14]

➤ Hot-water heat storage

It is the most favourable of the four storage types from the thermodynamic point of view because of the high specific heat of water and the high capacity rates for charging and discharging [14]. Furthermore, the storage efficiency of the tank can be improved by ensuring optimum stratification [5,10].

Water tanks are usually made of reinforced concrete and are partially embedded in the ground. The roof and the walls of the tanks are heat insulated, see Figure 1.13.



Figure 1.13: (A) Scheme of a solar-assisted district heating plant with seasonal heat storage. (B) Demonstration plant in Munich, 5700 m³, 2007 [17]

To avoid water vapour transfer through the concrete wall, and thus also protect the insulation from moisture and to reduce heat losses, an inner stainless steel liner is added to the wall. Over

the last few years, fibreglass-reinforced plastic has been studied as an alternative to concrete to reduce the specific costs [14].

➤ **Gravel/water heat store**

Gravel/water heat store is simply a pit with a watertight plastic liner which separates the storage material from the surrounding soil. The storage material is usually a mixture of gravel and water, but also sand and water, soil and water, or even layer combinations with these mixtures, see Figure 1.14. Heat is charged into and discharged out of the store either by direct water exchange or by plastic pipes installed in different layers inside the store [14]. Side-walls and roof are normally heat insulated.

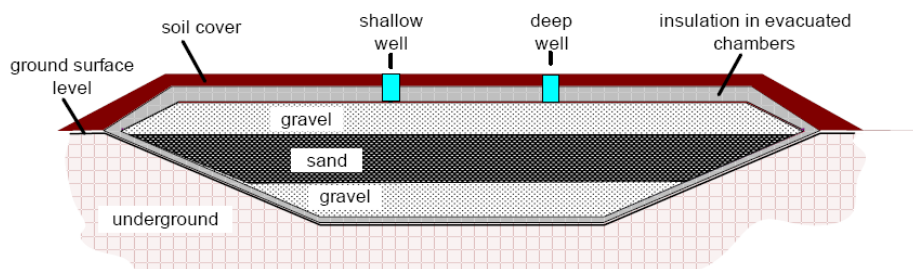


Figure 1.14: Newest generation of gravel/water TES in Eggenstein [18]

This technology appears as an alternative to reduce the construction costs of water tanks. However, since gravel/water mixtures have a lower specific heat capacity than water alone, the volume of the store has to be approximately 50% higher than a hot-water store to obtain the same heat capacity for the whole store.

➤ **Duct heat store or borehole storage**

Duct heat store consists of vertical heat exchangers installed inside a borehole, which ensures the transfer of thermal energy to and from the ground (clay, sand or rock). There are several types of heat exchanger and they are normally installed at a depth of between 30 and 100 meters, see Figure 1.15.

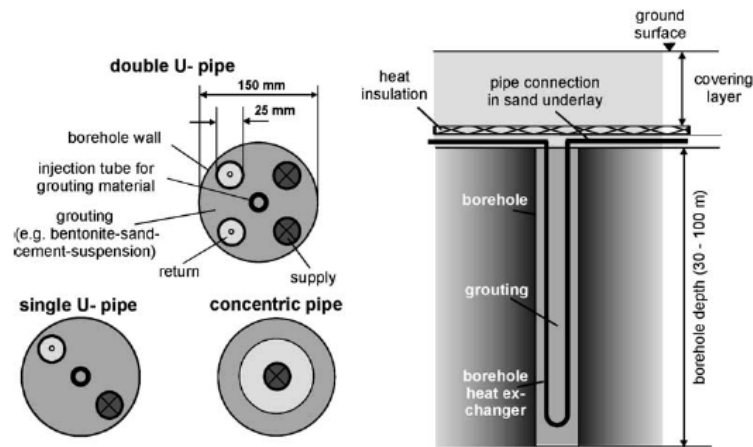


Figure 1.15: Types of borehole heat exchangers (left side) and sample installation [14].

A duct store requires less effort for construction than hot water or gravel-water heat stores, and it allows for modular design. Additional boreholes can be connected easily and the store can grow with the size of a housing district. However, the size of a duct store has to be between three to five times higher than that of a hot-water store to provide the same heat capacity. Besides, an additional buffer store is often required due to the lower capacity for charging and discharging [14].

➤ **Aquifer heat store**

An aquifer heat store uses water-saturated and permeable underground layers as storage medium. Thermal energy is transferred by extracting groundwater from the cold well and by re-injecting it into the hot well when it has been heated, see Figure 1.16.

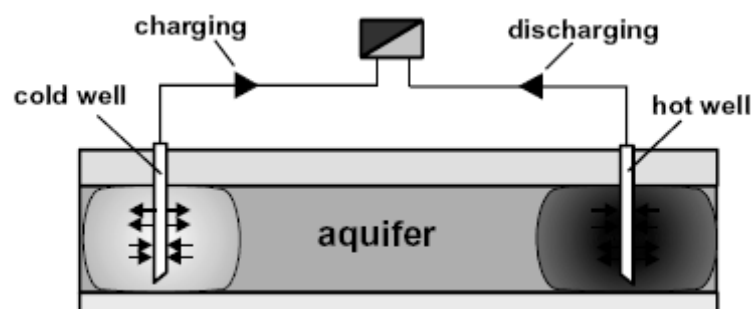
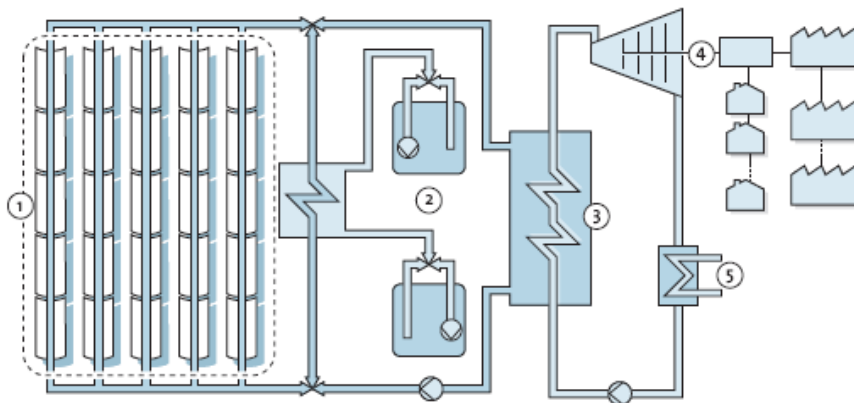


Figure 1.16: Scheme of an aquifer heat store [14]

A typical aquifer heat store works in the temperature range of 10-40 °C. Storing at higher temperatures (e.g., up to about 150 °C) was shown to cause many problems in experimental and pilot plants in the 1980s [10].

Solar Power Plants

As mentioned in the introduction, TES can be beneficial in a solar concentrator plant to store the excess solar energy generated during the daytime and use it at night or on cloudy days. This is the case of the current solar plant Andasol [19,20], installed in the province of Granada, Spain, see Figure 1.17.



1. Solar field, 2. Storage, 3. Heat exchanger, 4. Steam turbine and generator, 5. Condenser

Figure 1.17: Scheme of the solar thermal power plant, Andasol [19].

The plant uses a mixture of molten salts (NaNO_3 and KNO_3) as heat storage medium. This salt mixture is kept as a liquid in a cold storage tank at approximately $290\text{ }^\circ\text{C}$. When the heat supply exceeds the heat demand, the salt is heated to $390\text{ }^\circ\text{C}$ and pumped to a hot storage tank. Heat stored can then provide the necessary heat to operate the plant at night or during overcast periods.

1.2.1.2 Latent heat

1.2.1.2.1 Description

Another means of storing energy is by using phase change materials (PCM) or latent heat materials. When the PCM undergoes the phase change, it absorbs or releases a large amount of energy as latent heat. In fact, the energy density in the form of latent heat is much larger than in the form of sensible heat, which means lower volumes of materials need to be used. The phase change could be solid/liquid or liquid/gas: however, liquid/gas changes are not practical due to the large volume changes or high pressures required to store the materials in the gas phase.

Initially, the solid-liquid PCM behaves like sensible heat storage, i.e. heat is stored by raising the temperature of the material. When the temperature reaches the phase change the process becomes isothermal until all the material is transformed to the liquid phase. This makes latent heat especially useful for applications which operate in a narrow temperature range.

There are different classes of phase change materials involving inorganic and organic substances (Figure 1.18). Common substances are salts, hydrates, paraffins and fatty acids.

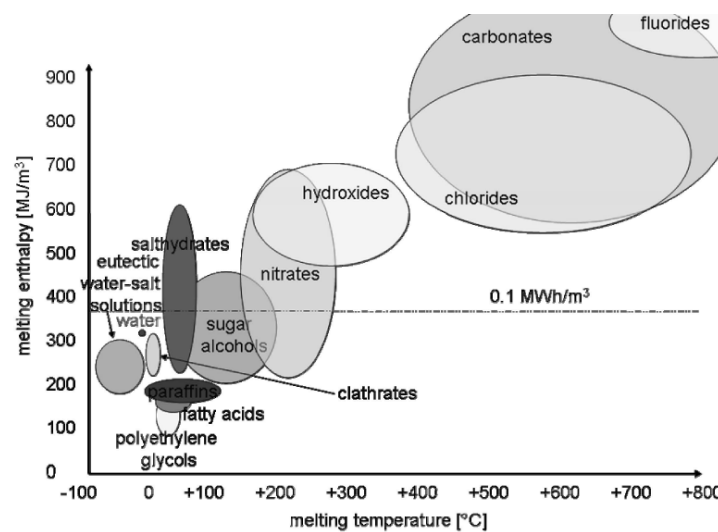


Figure 1.18: Classes of phase change materials at different temperature ranges [21]

A complete review of these materials and their properties can be found in Abhat [22], Lane [23,24], Kenisarin [25], Dinçer and Rosen [10], Zalba *et al.* [26], Farid [27], and Tyagi and Buddhi [28]. Based on these references among others, a full inventory of PCMs is given in Cabeza *et al.* [29] and H. Mehling and Cabeza [21]. More recent reviews have been carried out by Cabeza *et al.* [30] and Gil *et al.* [31].

The main advantages and disadvantages of organic and inorganic PCMs are reported in Table 1.5 [26].

Table 1.5: Comparison of organic and inorganic material for heat storage [26].

Organic	Inorganic
Advantages	Advantages
Non corrosives	Greater phase change enthalpy
Little or none subcooling	
Chemical and thermal stability	
Disadvantages	Disadvantages
Lower phase change enthalpy	Subcooling
Low thermal conductivity	Corrosion
Flammability	Phase separation
	Phase segregation, lack of thermal stability

1.2.1.2.2 Applications

PCMs have been used and are studied for various heating and cooling applications. Most of these applications are reviewed in [20,21,32]. However, so far the most studied and developed technology using PCMs is the incorporation of these materials into the building components such as walls, roofs and floors. By incorporating the PCM into the building material, the thermal inertia (thermal mass) of the building material can be increased, thereby smoothing the temperature fluctuations and reducing the heating and cooling demands. However, its uses as TES like replacing water tanks or in solar plants is still being investigated and no large demonstration plant has been built [20,31]. In addition, the cost of these PCM systems is substantially higher than the cost of sensible heat systems. Moreover, the long term stability of these materials is another important aspect for their application.

1.2.1.3 Sorption processes

1.2.1.3.1 Description

In sorption processes heat is not stored directly as sensible or latent heat but by way of a reversible physical or chemical process [33]. Figure 1.19 shows a schematic overview of the working principle.

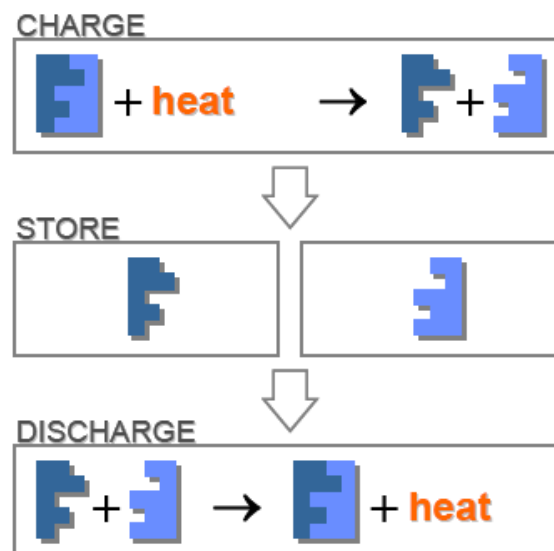


Figure 1.19: Working principle of a thermal storage system based on sorption process [33]

During the charging mode, heat is supplied and the thermochemical material dissociates into two components, which can be stored separately at ambient temperature. In the reverse step of storage

discharge, the two components are associated to form the original thermochemical material, thus releasing the stored heat.

Materials used in sorption storage have a much higher energy density than phase change materials or sensible heat materials. However, the relevance of storage systems based on sorption phenomena lies not only in their high energy density, but also in their negligible thermal loss, since as long as the two components are stored separately no reaction will occur. Therefore, it allows for effective long-term heat storage or even for heat transportation.

Storage systems based on sorption phenomena can be divided into open and closed systems [5,34], see Figure 1.20. On the one hand, in open systems the gaseous working fluid is directly released to the environment and thereby the entropy is released; therefore only water is a possible candidate as working fluid. On the other hand, in closed systems, not the working fluid itself but the entropy is released to the environment via a heat exchanger (condensation) [5]. An advantage of a closed system is that it can be used as a chemical heat pump for heating and cooling applications, or it can even be used to upgrade waste heat (e.g. industrial process) when it acts as a heat transformer (chemical heat pump).

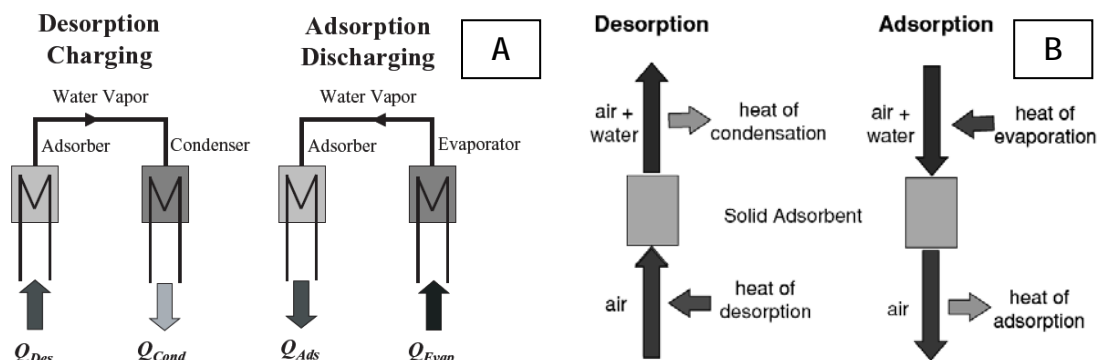


Figure 1.20: (A) Closed sorption system; (B) Open sorption storage system using a packed bed of solid adsorbent [34]

Two types of sorption processes can be distinguished: adsorption processes and absorption processes.

Adsorption

Adsorption process is the binding of a gaseous component on the inner surface of a porous material [34]. Depending on the nature of the bonding the process is classified as physical adsorption (physisorption) or chemical adsorption (chemisorption) [35].



Physical adsorption: Involves only relative weak intermolecular forces (van der Waals forces). The most common classes of solid adsorbents are zeolites, silica gels and activated carbon, while water, ammonia and methanol are commonly used as adsorbates [5,34,36-46]. These adsorbents are products of large-tonnage production (mainly for the needs of the chemical industry), and therefore, they are available, cheap, well-studied, and non-toxic [42]. In the last few years, new solid sorbents were developed to have a higher sorption capacity than the common ones, such as aluminophosphate (ALPO), silica-aluminophosphate (SAPO) and metal organic framework (MOF). However most of these novel materials are too expensive, especially for long-term storage [47].

Chemical adsorption: involves the formation of a chemical bond between the adsorbate molecule and the surface of the adsorbent and thereby, has a higher heat of sorption than physical adsorption processes. So far the chemical adsorption processes studied are those between metal salts with water, ammonia, methanol or methyl-ammonia as well as metal alloys with hydrogen [5,40-46,48,49].

Absorption

Absorption is a process in which a gaseous component enters the bulk of a liquid component. Traditional working pairs (adsorbate/absorbent), in absorption heat pumps, are ammonia/water (H_2O/NH_3) and water/lithium bromide ($H_2O/LiBr$) [41]. However, in the last years, some other working pairs have been studied for TES applications [50-52], such as water/sodium hydroxide ($H_2O/NaOH$), water/lithium chloride ($H_2O/LiCl$) and water/calcium chloride ($H_2O/CaCl_2$).

Further studies [53-56] have also focused on increasing the energy density of the salt solution by allowing the solution to reach the crystallization point (three-phase system). On the other hand, the complexity of the system is also increased.

1.2.1.3.2 Applications

Sorption processes can be used for several applications [5,36-49]. They allow for effective heat storage (short-/middle-/long-term) and transport due to the negligible heat losses. Moreover, they can be used as a heat pump for heat amplification, improving heat quality (heat upgrading) and refrigeration. In addition, they can work for a wide range of temperatures, generally from about $-50\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$. So, there is a large number of potential applications in the industrial, commercial, residential and transport sectors, and thus for energy savings and reduction of green-house effect.



Research for long-term solar heat storage has been mainly focused on physical adsorption processes and absorption processes [5,36,37,47,51]. So far, the studies that have been carried out on solar seasonal heat storage have demonstrated the feasibility of such systems but have ended up in chemical heat pumps or short-term storage machines for those with the highest performance [37]. In general, the current materials have not the correct properties (storage density/efficiency for a given discharging temperature), are too expensive, or have not yet been shown to work in prototypes under practical conditions. In addition, there are some other limitations related to technological difficulties (such as vacuum leakage, heat transfer, handling of crystallization, heat exchanger and reactor designs, etc.) and cost of components [5,36,37].

1.2.1.4 Chemical Reactions

1.2.1.4.1 Description

Heat can also be stored by means of a reversible thermochemical reaction. The working principle is similar to that of the sorption process:



First, in the charging period, chemical A is transformed into two new chemicals, B and C, because of heat absorption (endothermic reaction). Subsequently, the two new chemicals must be stored in separate vessels at ambient temperature. Second, in the discharging period, chemical B reacts with chemical C to form the original chemical A while releasing the stored heat (exothermic reaction).

The energy of thermo-chemical reactions is the highest of all the systems discussed here, and so it is the most compact way to store thermal energy.

So far, there are several types of reversible thermochemical reactions which have been studied the most:

- **Solid-gas reaction:** Hydration and carbonation of metal oxides to hydroxides and carbonates, respectively [57-62].
- **Liquid-gas reactions:** Hydrogenation of acetone to 2-propanol [63-66], benzene to cyclohexane [67], and acetaldehyde to ethanol [68-70], hydration of isobutene to *tert*-butanol [71,72], and polymerization of acetaldehyde to paraldehyde [73].



- **Gas reactions:** Reforming of methane with carbon dioxide or steam and synthesis of ammonia [74].

Nevertheless, there are a large number of chemical reactions that have been proposed over the last decades and that can be found elsewhere [57,74,75].

1.2.1.4.2 Applications

Like sorption systems, chemical reactions can be also used for heat storage (short-/middle-/long-term), transport or also as a heat pump for heat amplification, improving heat quality (heat upgrading) and refrigeration. In addition, chemical reactions extend the temperature range for heat storage, allowing us to store high grade heat (>400 °C) besides low and medium grade heat. Therefore it allows for important energy savings as the waste heat lost from many industrial applications and power plants is medium and high grade heat (207).

Although, chemical reactions are suitable for long-term solar heat storage, most of them have been studied or proposed for short- and medium-term heat storage.

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2 Scope

2.1 Recycling of waste: Tannery Industry

The objective of this work is to treat chromium(III) containing leather waste in order to isolate high added collagenic biopolymers and to recover and re-use of the chromium(III) present on the solid tanned wastes as well as on the tannery's effluents.

To accomplish the aforementioned objective, several studies were performed:

- The optimization of the novel dechroming process, based on the oxidation with peroxides (specifically hydrogen peroxide) in alkaline medium. To fulfil the optimization, a mathematical experimental Box-Hunder design was performed on two complementary treatments:
 - **Dechroming of chromium(III):** Experimental mathematical Box and Behnken design in function of pretanning formaldehyde (HCHO), alkaline medium (Na_2CO_3); hydrogen peroxide (H_2O_2) and time as the most significant variables. The experimental factors and their interactions were analyzed on the residual chromium(III) and on the efficiency. Finally, a desirability function was used in order to reach the best experimental conditions for both Efficiency and residual Chromium.
 - **Isolation of collagenic biopolymers:** Experimental mathematical Box-Hunter Design in function of main variables, such as: macerator (NaOH), activators (H_2O_2), time and temperature; in order to obtain a new bioproduct from dechromed collagenic wastes.

Additionally, a financial study of the overall installation and the corresponding cost in obtaining the new chemical products was performed.

- An alternative process to recover tannery-chromium(III) effluents was developed. In this process the same oxidation reaction is applied in order to completely oxidize the chromium(III) present in the effluents to chromium(VI) followed by two sequential steps; a) fixation into a ion-exchange resin and, b) reduction to chromium(III) in a batch combined system. The objective is to study the influence of factors that affect the selectivity of the resin and the influence of several reducing agents on the yield of chromium(III) recovered.



2.2 Thermal energy storage: built environment

The objective of the current thesis is to find a suitable thermochemical material (TCM) for seasonal solar heat storage in the built environment. The seasonal solar heat storage system is intended to cover the space heating demand of a low energy house during the winter months without available solar energy. The requirements and constraints of the current system are: a medium temperature collector (vacuum tube) is used to dehydrate the salt hydrate. It is assumed that these collectors can deliver heat at a maximum temperature of 150 °C. During the winter, the water vapour is supplied by an evaporator condenser connected to a borehole heat exchanger at 10 °C. This means that a saturation water pressure at 10 °C [$P_{\text{H}_2\text{O}}^{\text{sat}}(10^\circ\text{C})$] is available during hydration in winter

To achieve the aforementioned objective, several studies were performed:

- A review of the experimental research on thermal energy storage system with TCM under practical conditions. The objective of this work was to provide required background and knowledge for the development research.
- The experimental characterisation of magnesium sulphate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) as promising material for seasonal solar heat storage in the built environment. The objective of this work was to determine the suitability of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ for application in a seasonal heat storage system for the built environment. The dehydration and hydration of the material was studied at atmospheric pressure. However, the results of this study indicated that the application of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at atmospheric pressure is problematic for a solar heat storage system where heat is released above 40 °C using a water vapour pressure of 1.3 kPa. A separate experiment performed in a closed system at low pressure indicated that a small amount of heat can be released at 50 °C and a water vapour pressure of 1.3 kPa.
- Therefore, further experiments were conducted to study the effect of lowering the system pressure on water uptake, and thus determine the suitability of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ for application in a seasonal heat storage system for the built environment. Additionally, the salt hydrates of aluminium sulphate octadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were also studied as potential TCM. It was found that the chlorides can deliver heat to the residential heating system at a higher temperature than the sulphates.

3 Transformation plant for converting chromium(III) waste into chemical products for the leather industry

3.1 Introduction

Chapter II shows the work performed for the optimizations of a quick procedure for the complete dechromation of chromium(III) waste. This procedure is based on the oxidation of chromium(III) to chromium(VI) through the action of hydrogen peroxide in an alkaline medium. The highly toxic chromium(VI) which is produced is stored in a stainless steel tank, before being subsequently reduced to chromium(III) that can be reused in the tanning process. The oxidation reaction, at room temperature, leads to the formation of peroxochromates that have great oxidizing power and which significantly accelerate the pre-hydrolysis, this corresponding to the maceration stage in the gelatine production process. In this way, gelatine or any other type of collagen biopolymer can be obtained in a single stage and with an excellent yield.

The main advantages of this procedure lie in the fact of a high-speed oxidation reaction which can be set up in an average of 1 hour. This means considerable economic savings in terms of operating cost (chemicals, energy, labour, time, etc.). It should be stressed that other process such as change of pH (acid/alkaline), alkaline-based enzymatic, and/or other masking-based chemicals compounds take over 6 hours [1-4]. Additionally, unlike previous process, the oxidation of chromium(III) to chromium(VI) using peroxides, generally hydrogen peroxide, in an alkaline medium allows to obtain collagen fibres of leather with very little residual chromium(III) and, with their physical and chemical characteristics completely unaffected. By means of this process, the chromium(III) collagen fibres are left at a stage previous to the tanning phase, remaining in the raw or pickle stage, not established or crosslinked [4-6].

As previously described, the whole process involve the following stages:

- Grinding process.
- Dechroming process.
- Centrifuge operation.
- Isolation of collagen biopolymers.
- Storage.

In this chapter, an experimental mathematical model is developed to study the degree of significance of the most important variables as well as to study the corresponding interaction between variables in the process established to obtain new types of biopolymers. Therefore, the experiment can be rationalised and a mathematical model can be used to control the whole process and to determine the optimum zone in each case. Furthermore, the research also aims to carry out a financial study of the overall installation and the corresponding cost in obtaining the new chemical products.

3.2 Contribution to the body of knowledge

The aim of this work is first to solve an important environmental problem faced by the leather industry, which incurs significant costs in managing this type of waste; and second, to enable acceptable financial gains in terms of obtaining chemical products designed for the tanning industry. These products are: basic chromium(III) salts from the chromium(III) waste, collagen biopolymers suitable for retanning, filling basifying, delimiting and glazing finishes that can partially or totally replace casein.

The main novelties introduced in the industrial plants are:

- **Size reduction by grinding:** when processing these types of wastes, it is essential to submit them to a size reduction operation (defibrering) to achieve a fibre size between 1 to 5 mm of sieve diameter. In this way, it is possible to reduce the concentration of chemicals compounds employed, and lower the reaction temperature.
- **Formaldehyde crosslink of chromium(III) wastes:** Stabilization with formaldehyde allows the elimination of sodium sulphate (in alkaline medium) and sodium chloride (in acidic medium), and prevents dechromed collagen fibres from swelling and hydrolyzing during the dechroming and subsequent treatments.
- **Elimination of the ion exchange equipment:** the hexavalent chromium can be removed using an anion exchange resin and reduction, in situ, with hydrogen peroxide in acidic medium [7,8]. A very concentrated solution of chromium(III) is obtained and with final adjustment to the right basicity, offers the possibility to be reused back to tannery. Nevertheless, in order to reduce the investment cost in the equipment of a global pilot-plant installation, it was suggested to eliminate this unit and the collected chromium(VI) effluent produced by this procedure was stored into a stirred stainless steel tank where the same reduction process took place. Although the chromium(III) content is rather low (0.4 %), a calculated amount of solid commercial

chromium(III) basic salt can be added to this effluent; so it can be ready to be used in the tanning operation.

- **Recommended Physical State of the Isolated Biopolymers:** The biopolymers obtained according to this process can be prepared either in a completely dry state or in a solution of 30 % concentration. Referring to the first option the investment cost is considerably higher due to the Spray Drier equipment. Therefore, it is recommended to use the 30 % solution; however, it has to bear in mind that at this concentration and in function of the temperature, e.g.: below 14 °C this biopolymer will be converted in a solid-jelly product that will need to be heated up. It would be advisable to use a jacketed stainless steel storage tank in order to heat it up around 40 °C, so the biopolymer solution will easily become lightly viscous and therefore can be poured into the drum or other vessel.

The mathematical experimental design was performed on two complementary treatments: dechroming of chromium(III) and isolation of collagenic biopolymers. In order to evaluate the significance of the experimental factors and their interactions on the residual chromium(III) an analysis of variance has been performed. Factors and interactions that have not been reached a minimum significative level of 10% have been removed from the model.

- **Dechroming process:** Experimental mathematical Box and Behnken design [9] in function of pretanning formaldehyde (HCHO), alkaline medium (Na₂CO₃); hydrogen peroxide (H₂O₂) and time as the most significant variables. The experimental factors and their interactions were analyzed on the residual chromium(III) and on the efficiency. Finally, the optimal desirability satisfies a combined answer with minimal residual Chromium(III) and maximal efficiency.
- **Isolation of collagenic biopolymers:** Experimental mathematical Box-Hunter Design [10] in function of main variables, such as: macerator (NaOH), activators (H₂O₂), time and temperature; in order to obtain a new bioproduct from dechromed collagenic wastes. The influence of the Temperature, time, concentration of NaOH and mL of H₂O₂ on the Bloom degrees was adjusted using the following second-order polynomial function:

$$Y = b_0 + \sum_i b_i X_i + \sum_{ij} b_{ij} X_i X_j; \quad \text{for } i \geq j$$

where b_0 is the independent term directly related with the mean value of the experimental plan, b_i are the regression coefficients which explain the influence of the variables in their linear form, and

b_{ij} are the regression coefficients that account for the influence of the variables in their quadratic form, which could define optimum zones and possible interactions between them [10,11].

It has to be taken into account that only NaOH concentrations and temperature were the variables that showed significant influence on the Bloom. Therefore, based on the previous results, a second cycle of experiments was designed using the Evolutionary Operation (EVOP) technique in order to reach the optimum. Finally, the isolated collagenic biopolymers were tested, either on lab-scale or pilot plant, for several industrial applications, obtaining excellent results.

The final contribution to the body of knowledge is the financial study of the overall installation and the corresponding cost in obtaining the new chemical products.

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4 Alternative process for recovery of chromium(III)-effluents

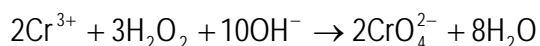
4.1 Introduction

Based on the previous process [1] (Chapter II), a similar process with slight changes can be used to recover chromium(III) from waste effluents. Traditionally tanneries used the alkaline precipitation method (magnesium oxide) of chromium(III) as the recovery method. This technique may in fact be the cheapest treatment nowadays; however, latest accurate economic studies have revealed the influence of some parameters that could alter significantly the investment cost; thus opening a door to other alternative processes. The main problems that the precipitation technique brings along are the following (conventional treatment):

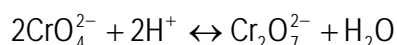
- The presence of highly masked chromium(III) complexes, difficult to precipitate even in alkaline medium.
- The speed of precipitation and the density of the precipitate can be an important problem. Sometimes, the application of heat is required.
- Filtration of the precipitate and subsequent drying out until 30% water content of the chromium(III)-cake (different techniques are used).
- Recovered chromium(III) obtained by redissolving the cake with sulphuric acid and final adjustment to 33 °Sch basicity can mostly occlude highly masked chromium(III) complexes which in turn, produce a uneven dyed grain surface of leather; therefore, limiting dyeing to dark shades.

Furthermore, energy consumption, rather long time dependence of the overall process, simple but numerous stages, and limited coverage fashion catalogue colours have been the basis to offer a possible new alternative process.

Therefore, Chapter III aims to recover the chromium(III) from wastewater coming from the various chromium(III) using processes and, at the same time, to obtain an effluent that can be used directly without complementary treatments. The wastewater containing chromium in the two forms, trivalent and hexavalent, is first filtered to ready for the following oxidation step which has the purpose of converting all the chromium to the hexavalent form in order to allow its retention by the anionic exchange resin. The oxidation is carried out with hydrogen peroxide in alkaline medium (NaOH, pH=12). This reaction only forms water as shown in the following reaction [2]:



The chromium(III) recovery process is based on ion exchange where dichromate anions are fixed in the resin. In this phase, chromium(VI) is in the chromate form. However, it is better to load chromium(VI) in the dichromate form because for each possible site on the resin two chromium atoms can be fixed instead of one. Therefore prior to adding the column load, the wastewater is acidified in order to form the dimer (orange colour), instead of the yellow chromate, using a final pH between 3.5 and 4:



If pH is less than 4, the previous reaction is displaced to the right and we can proceed to load the column with the exchange resin.

The reduction process of the fixed chromium(VI) in the resin enable to obtain a concentrated chromium(III) liquor using the smallest possible quantity of reducer by substitution of the dichromate fixed in the resin by another anion, at the same time, reducing the dichromate to trivalent chromium. The reaction takes place in the column used for the dichromate exchange.

4.2 Contribution to the body of knowledge

Chapter III presents a process to recover tannery chromium(III) effluents alternative to the conventional precipitation one. This process is based on the oxidation of chromium(III) to chromium(VI), followed by two sequential steps:

- Fixation into an ion-exchange resin.
- Reduction to chromium(III) in a batch combined system.

For ion exchange to be effective, it is necessary that the attraction of the selected ion to the resin is at a high level. Additionally, a number of factors affect the selectivity of the resin, of which the following are of the most interest in this study:

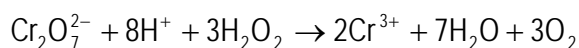
- **Temperature:** The resin deteriorates and loses its capacity when there is an abrupt temperature change [3]. During the resin regeneration phase and in the Cr(VI) to Cr(III) reduction, a great quantity of heat is generated reaching very high temperatures, especially in cases where the quantity of fixed dichromate is large.



- **Contact time:** It is important that the resin and the solution have an adequate contact time; avoiding short contact times, this has a major importance to avoid waste of the resin.
- **Resin distribution:** When the resin is loaded in the column, the excess water is evacuated assuring that there is no dryness during any moment of the process because repeated cycles of drying and rehydration generate tensions (similar to those in osmotic crashes) and can lead to the resin breakage. Also, the resin bed should be free of air pockets as this causes the effluent to pass by easier routes.
- **Resin preparation:** The resin should be mixed and washed with water to eliminate materials resulting from storage. The wash needs to be acidic, to ensure that the exchange resin is an active ionic form. We chose Amberlite IRA-96 [4] which is an excellent macroporous resin suitable for fixing dichromate and resistant to the reduction reaction in a recycling process.

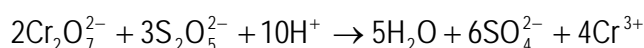
For the reduction stage, three reducing agents were used: The selection of these reducing agents was carried out by bibliographic research:

- **Reduction with hydrogen peroxide:** The reducer agent used is hydrogen peroxide in acid medium. The reaction that takes place is presented in the following equation:



The empty sites previously occupied by the dichromate are now filled by sulphate groups from the added sulphuric acid. The liquor obtained is sufficiently concentrated and rich in sulphates. The reaction in the column can be controlled visually as it forms a front that gradually changes from orange to green. The next step is to carry out series of washes with water and dilute sulphuric acid to recover the maximum quantity of chromium, and at the same time, to regenerate the resin.

- **Reduction with sodium bisulphate:** The method for preparing recovered chromium(III) liquor with bisulphite is very similar to that using sulphite. In this case, bisulphite reacts with acid forming the sulphite which then acts as reducer and yields greater quantities of sulphates. The next equation shows the overall reaction:



This reduction generates a large amount of complex and neutral salts. The experience shows that the reaction could be developed in the cold and is also possible without using sulphuric acid.



- **Reduction with glucose:** This is one of the most widely used reduction methods used in chromium(III) recovery. In this reaction, glucose is not completely oxidized to carbon dioxide, but intermediate compounds are formed, generally organic acids that play a role, their influence diminishing the basicity and having a masking effect on the chromium. The following equation shows the reaction when the glucose is completely oxidised:



This form of the process is significant because of the tanning properties of the resulting liquors. The masking effect increases as the quantity of glucose is increased, favouring the formation of organic acids. In contrast, temperature reduction diminishes the basicity. One problem that arises with this method is the doubt about whether it is better to add glucose to the acid-dichromate mix or to add acid to the glucose-dichromate mix.

So, this work presents the influence of all these parameters or factors on the chromium(III) recovered. It should be pointed out that 97 % of chromium(III) was recovered by this method when using hydrogen peroxide as reducing agent.

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5 Thermochemical energy storage and conversion: a review of the experimental research under practical conditions.

5.1 Introduction

Chapter V gives a review of the experimental research on chemical sorption process and chemical reactions based on solid-gas systems over the last two decades. As mentioned earlier, the increase interest for chemical sorption process and chemical reactions for TES applications lies in the fact that they offer the high energy density of the materials involved (important when the volume is limited), and allow for long-term storage due to the negligible heat loss. In addition, they can cover a wide range of working temperatures; usually chemical sorption processes are used to store and convert low grade heat ($< 100\text{ }^{\circ}\text{C}$) and medium grade heat ($100\text{-}400\text{ }^{\circ}\text{C}$) whereas chemical reactions are used to store and convert medium and high grade heat ($>400\text{ }^{\circ}\text{C}$). Therefore, they can be used for a wide range of applications and thereby contributing to substantial energy savings and reduction of the greenhouse effect.

Furthermore, chemical heat pumps (CHP) or heat transformers (HT) have several advantages to that of traditional vapour-compression heat pumps (mechanical energy). In addition to the benefit of being driven by waste heat, they utilize refrigerants with zero ozone depletion and global warming potentials, i.e. no chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC), and, they are noise and vibration free, long lasting [1,2].

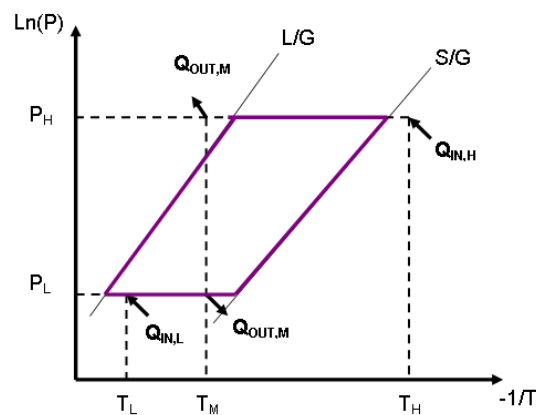


Figure 5.1: Working principle of a chemical heat pump

The basic CHP system comprises a solid-gas reactor coupled with a condenser/evaporator. The working principle is illustrated in Figure 5.1 in a Clausius-Clapeyron's diagram, wherein the solid-gas (S/G) and liquid-gas (L/G) equilibrium lines are given by the equation:

$$\ln(P_{eq}) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

The chemical heat pump system operates in two successive phases (thermal conversion) or with a time gap (thermal storage mode): charging phase (also named regeneration, decomposition or desorption) and discharging phase (also named production, synthesis or sorption).

The charging phase occurs at high pressure (P_h). Heat at high temperature (T_h) is supplied to the reactor and the solid (S) decomposes. The gas (G) released from the decomposition is condensed by rejecting heat from the condenser at medium temperature (T_m). By contrast the discharging phase (reverse phase) occurs at low pressure (P_l). The liquid evaporates by absorbing heat at low temperature (T_l) and the synthesis heat is released at T_m . In both phases the synthesis and decomposition occurs when the salt is removed from its equilibrium of temperature (equilibrium temperature drop, ΔT) and pressure (equilibrium pressure drop, ΔP) for heat and mass transfer [3-6].

The basic cycle shown in Figure 5.1 can be used to produce refrigeration at T_l and/or to produce heat at T_m . However the two phases can be interchanged to operate the cycle as a heat transformer and thus upgrade heat from T_m to T_h . In this case the charging phase occurs at low pressure (P_l) and the discharging phase occurs at high pressure (P_h). Furthermore, in CHP systems that implies the use of non condensable gases or that uses a condensable gas, but where the safety problem regarding to the high pressure becomes an issue (legislators), the evaporator/condenser is replaced by another reactor [1,7,8]. In sorption processes, the CHP systems using two reactors are also known as resorption systems.

The figures of merit which are commonly used to characterise the performance of a CHP are the coefficient of performance (COP), or COP of amplification for the heating effect (COPA), and the specific cooling/heating power (SCP/SHP).

5.2 Contribution to the body of knowledge

Chemical adsorption process and solid-gas reaction opens a new way for seasonal heat storage in the built environment. Nevertheless, these thermochemical materials have been studied for many years in

other thermal energy storage applications, and therefore a review is fundamental to provide the required background and knowledge for the development research.

So, in this Chapter V is given a review of the experimental research on chemical sorption process and chemical reactions over the last two decades. The main contributions to the body of knowledge can be summarized in the following points:

- Overview of the current thermochemical materials (TCM) used for thermal energy storage and conversion applications (Figure 5.2).

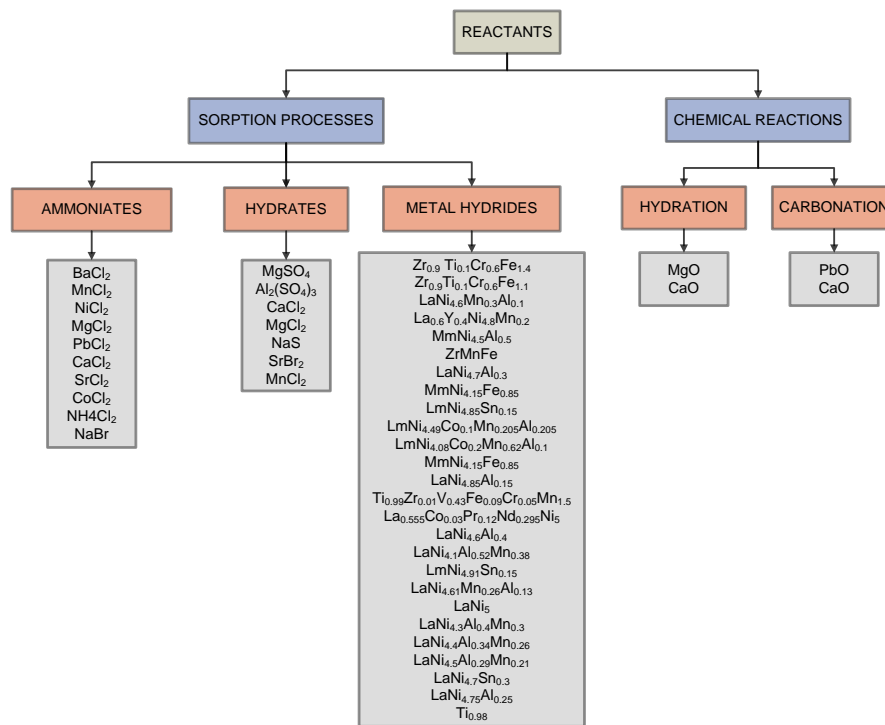


Figure 5.2: Overview working pairs tested in prototypes under practical conditions

- Main bottlenecks or limitations found in chemical adsorption process and chemical reactions based on solid-gas systems (for its commercial application).
 - Poor heat and mass transfer performance (low thermal conductivity [9-12], the bad heat transfer between the solid bed and the reactor (heat exchanger) wall [13] and the swelling and agglomeration phenomena occurring during the sorption process with ammonia or water [14-16]).
 - The thermodynamic cycle operation require of large temperature swings of the sorption reactor during the process which reduces the efficiency (COP) of the system [13,17].

- Proposed solutions
 - Reactor design
 - Composite materials, which are mainly aimed to improve the poor heat and mass transfer performance in the reactive bed.
 - Advanced cycle concepts, which are mainly designed to increase the efficiency and power output of the process with a better heat management and mass recovery strategies.
- Applications
 - Cooling applications: refrigeration, air conditioning, freezing and deep-freezing
 - Heating applications: air heating, drying, steam generation, etc.
- Overview of the experimental performance of those materials under practical conditions.
 - Cooling technologies: reported values for the SCP are in the range from 100 to above 1000 W·kg⁻¹ and for COP vary from 0.2 to 0.65.
 - Heating technologies: reported values for SHP are in the range from 100 to 300 W·kg⁻¹.

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CHAPTER V

Thermochemical energy storage and conversion: A review

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6 Characterisation of MgSO₄ Hydrate for Thermochemical Seasonal Heat Storage

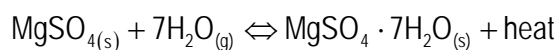
6.1 Introduction

In this Chapter VI is studied the behaviour of a selected chemical sorption process or chemical reaction suitable for seasonal solar heat storage in the built environment. The selected thermochemical material (TCM) must be capable to fulfil the space heating and domestic hot water demands ($T \geq 40$ °C) of a low energy house during the two winter months without available solar energy.

One contribution to the body of knowledge from the previous Chapter V was to provide an overview of the TCMs research for thermal energy storage and conversion in heating and cooling applications based on the last twenty years. Nevertheless, not all the chemical sorption processes and chemical reactions are suitable for seasonal solar heat storage in residential areas. Some of the requirements and constraints for such application are summarized in the following points [1]:

- High storage density ($> 2 \text{ GJ} \cdot \text{m}^{-3}$)
- The compounds involved in the chemical sorption process or reaction need to be:
 - Chemically stable
 - Safe and easy to handle
 - Recyclable and environmentally benign (non toxic)
 - Inflammable
 - Cheap
- The chemical reaction or chemical sorption process need to be:
 - Controllable
 - Take place at temperature levels within the range of domestic solar collectors (< 250 °C).
 - Take place at or below atmospheric pressure (safety).

So, based on these criteria, a previous theoretical study [2] identified magnesium sulphate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) as promising material for seasonal solar heat storage in residential areas, by means of the following reaction:



The theoretical energy density of MgSO₄·7H₂O is 2.8 GJ·m⁻³.

The starting point of the investigation was that the material should be able to store and release solar heat under practical conditions. During the summer a medium temperature collector (vacuum tube) is used to dehydrate the salt hydrate. It is assumed that these collectors can deliver heat at a maximum temperature of 150 °C. During the winter, the water vapour is supplied by an evaporator condenser connected to a borehole heat exchanger at 10 °C. This means that a saturation water pressure at 10 °C [$P_{\text{H}_2\text{O}}^{\text{sat}}(10^\circ\text{C})$] is available during hydration in winter.

In order to determine the suitability of MgSO₄·7H₂O for application in a seasonal solar heat storage system, the dehydration (charging) and hydration (discharging) behaviours of the material were studied by means of the following techniques:

- **Thermal Analysis:** Thermal analysis was used to obtain information on the dehydration and hydration behaviours of the material at atmospheric pressure (1 atm). Two thermal analysis techniques were used in this work: differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. TG analysis involves the measurement of the mass change as a function of temperature or time, and DSC involves the measurement of heat (enthalpy) changes as a function of temperature or time, in which both are subjected to a predefined temperature program.
- **X-Ray Powder Diffraction:** Information on the crystal structure of the different hydrates of magnesium sulphate before, during, and after dehydration and hydration was acquired using X-ray powder diffraction.
- **Scanning Electron Microscopy:** Microstructural changes on the grain level were observed using a JEOL JSM 6330F scanning electron microscope (SEM).
- **Particle Size Distribution Measurements:** The effect of hydration and dehydration on the particle size distribution was investigated using a Malvern Master 2000.

6.2 Contribution to the body of knowledge

In this Chapter VI, measurements are presented, which will give information on whether MgSO₄·7H₂O can be dehydrated using a medium temperature collector and whether the dehydrated material is able to release the stored heat under practical conditions.

The main contributions to the body of knowledge are:

- MgSO₄·7H₂O can be dehydrated at temperatures below 150 °C, a temperature that can be reached by a medium temperature collector (vacuum tube).
- The material was able to store 2.2 GJ·m⁻³ (based on the solid density of MgSO₄·7H₂O), almost nine times more energy than can be stored in water as sensible heat (0.25 GJ·m⁻³ in the temperature range from 25 to 85 °C).
- On the other hand, the experimental results indicate that the release of the stored heat is more difficult; under practical conditions (partial water pressure of 1.3 kPa and T>40 °C), the material is not able to take up water at atmospheric pressure.

A separate experiment was performed using a fixed-bed reactor to test the hydration behaviour of magnesium sulphate at low pressure (closed system) and under the aforementioned operating conditions. The initial test using a closed fixed-bed reactor operating at low pressure showed a maximum temperature increase of 4 °C. This result indicates that under low-pressure conditions dehydrated material is able to react with water under practical conditions. Further experiments have to be conducted to study the effect of lowering the system pressure on water uptake.

6.3 References

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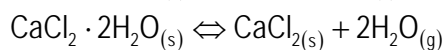
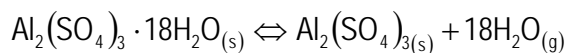
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7 Characterisation of salt hydrates for compact seasonal thermochemical storage

7.1 Introduction

As seen in Chapter VI, the amount of water taken up and the energy released by magnesium sulphate turned out to be strongly dependent on the water vapour pressure, temperature, and the total system pressure. The results indicate that the material is not able to take up water at atmospheric pressure; however, the first experiments performed in a closed system at low pressure indicate that a small amount of heat can be released at 50 °C and a water vapour pressure of 1.3 kPa [1]. Therefore, in Chapter VII, the hydration behaviour of magnesium sulphate was further studied in a closed system at low pressure.

Furthermore, an internal research was performed to identify other potential alternative thermochemical materials for seasonal solar heat storage in the built environment. These are the reversible hydrations of aluminium sulphate octadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), respectively.



The theoretical energy density of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ are 2.75, 2.48 and 1.44 $\text{G} \cdot \text{m}^{-3}$, respectively.

The hydration behaviour of the selected TCMs were also studied in a closed system at low pressure. The experimental test-rig consisted of a fixed-bed reactor connected to an evaporator condenser.

7.2 Contribution to the body of knowledge

In this Chapter, measurements are presented, which will give information on whether the materials can be dehydrated using a medium temperature collector and whether the dehydrated materials are able to release the stored heat under practical conditions.

The main contributions to the body of knowledge are:

- The temperature lift of the bed measured during the hydration was found to be dependent on the type of salt; under identical conditions, the chlorides (calcium chloride and magnesium chloride) show a larger temperature lift ($\Delta T=11-19$ °C) than the two sulphates (aluminium sulphate and magnesium sulphate, $\Delta T=1-4$ °C).
- Therefore, under practical conditions, the chlorides can deliver heat to the residential heating system at a higher temperature than the sulphates. Nevertheless, it should be pointed out that, due to the highly hygroscopic nature of the chlorides, these materials tend to overhydrate transforming to a sol-gel like structure (deliquescence).

7.3 References

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Pages from 137 to 143 provide the following paper:

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8 Results

8.1 Transformation plant for converting chromium(III) waste into chemical products for the leather industry

8.1.1 Statistical treatment of the results

Dechroming process

Efficiency and residual chromium(III) of the 27 experiments developed according to the Box and Behnken design for four factors was analysed. Factors, ranges and units are shown in Table 8.1.

Table 8.1: Factors, range and units used for the experimental mathematical Box and Behnken design

Factor	Low level	High Level	Units
HCHO	0.0	2.0	% w/fibre
Na ₂ CO ₃	2.0	8.0	% w/bath
H ₂ O ₂ 110vol	2.0	10.0	% w/bath
Time	30.0	90.0	min

In order to evaluate the significance of the experimental factors and their interactions on the residual chromium(III) and on the efficiency Analysis of Variances were performed.

a) Residual Chromium

In order to evaluate the significance of the experimental factors and their interactions on the residual chromium(III) and on the efficiency Analysis of Variances were performed (Table 8.2). Factors and interactions that have not been reached a minimum significant level of 10% have been removed from the model.

Table 8.2: Analysis of variance for residual chromium(III) (R-squared: 97.1928 %)

Source	Sum of squares	Df	Mean Square	F-ratio	P-value
A:HCHO	52801.3	1	52801.3	3.07	0.0959
B: Na ₂ CO ₃	142790	1	142790	8.3	0.0096
C: H ₂ O ₂ 110 vol.	8.68E+06	1	8.6819E+06	504.75	0.0000
D: time	99372	1	99372	5.78	0.0266
AC	79242.3	1	79242.3	4.61	0.0450
CC	1.97E+06	1	1.97188E+06	114.64	0.0000
DD	59662.8	1	59662.8	3.47	0.0781
Total error	326810	19	17200.5		

All factors were found to be highly significant, especially the oxygen peroxide concentration at linear and quadratic components that were significant at 0% level. The linear component of the Na_2CO_3 concentration was also significant at 0.96%, and the time in its linear and quadratic components was significant at the 2.7 and 7.8% respectively. Lastly the linear component of the HCHO was significant near at the 10% level, although an interaction between the HCHO and the H_2O_2 is significant at 4.5%.

The evolution of the residual chromium(III) according to the variable levels can be modelled by the following equation:

$$\begin{aligned} Cr_{\text{res}} = & 2970.34 + 277.458 \cdot [\text{HCHO}] + 36.3611 \cdot [\text{Na}_2\text{CO}_3] \\ & - 593.763 \cdot [\text{H}_2\text{O}_2] + 9.84028 \cdot [t] - 35.1875 \cdot [\text{HCHO}] \cdot [\text{H}_2\text{O}_2] \\ & + 34.6921 \cdot [\text{H}_2\text{O}_2]^2 - 0.10728 \cdot [t]^2 \end{aligned}$$

The equation (1) explains the 97 % of the squared variation of the residual chromium(III).

b) Efficiency

Using the same methodology the influence of the three factors (HCHO, Na_2CO_3 and H_2O_2) on the efficiency was examined (Table 8.3). Non significant effects and interactions were removed and the significant effects are those shown in the following table of the analysis of variance.

Table 8.3: Analysis of variance for efficiency (R-squared: 80.0834 %)

Source	Sum of squares	df	Mean Square	F-ratio	P-value
A:HCHO	887.004	1	887.00	23.16	0.0001
B: Na_2CO_3	546.885	1	546.89	14.28	0.0012
C: H_2O_2 110 vol	638.604	1	638.60	16.68	0.0006
AA	374.917	1	374.92	9.79	0.0053
AC	482.901	1	482.90	12.61	0.0020
BC	149.206	1	149.21	3.9	0.0624
Total error	765.868	20	38.29		

It was found that HCHO, H_2O_2 and Na_2CO_3 are a highly significant; as the concentration increases the efficiency also increases. Nevertheless being that the quadratic effect of HCHO is significant an optimal concentration of HCHO can be observed. Two interactions were significant (HCHO x H_2O_2 and H_2O_2 x Na_2CO_3). According to the effect of the first one it seems that at high H_2O_2 concentrations the presence of HCHO improves the efficiency, while at low H_2O_2 concentrations no effect of HCHO on efficiency was pointed out. The second interaction shows that at low concentrations of H_2O_2 no



effect of Na_2CO_3 was observed on the efficiency, while at high concentrations of H_2O_2 the Na_2CO_3 improves the efficiency.

$$\begin{aligned} \text{Efficiency} = & 105.474 + 7.11458 \cdot [\text{HCHO}] - 0.803472 \cdot [\text{Na}_2\text{CO}_3] \\ & - 7.11542 \cdot [\text{H}_2\text{O}_2] - 2.74688 \cdot [\text{HCHO}] \cdot [\text{H}_2\text{O}_2] - 7.49917 \cdot [\text{H}_2\text{O}_2]^2 \\ & + 0.508958 \cdot [\text{Na}_2\text{CO}_3] \cdot [\text{H}_2\text{O}_2] \end{aligned}$$

The equation explains the 80.1% of the squared variations of the efficiency. Non significant influence of the time over the efficiency was observed.

c) Optimization

In order to reach the best experimental conditions for both efficiency and residual chromium(III) the desirability function was used. The optimal zone was obtained at approximately 1.92 % of HCHO, 6.36 % of Na_2CO_3 , 9.77% of H_2O_2 110 vol and high level of time (90 minutes). The optimal desirability satisfies a combined answer with minimal residual chromium(III) (603.34 ppm) and maximal efficiency (99.99 %)

Furthermore, it was found that small variations on the concentration of HCHO and Na_2CO_3 in the optimal zone could not produce significant variations on desirability, although a decrease of H_2O_2 shall produce a great decrease of desirability, i.e. a fast deviation from the optimal conditions where minimal residual chromium(III) and maximum efficiencies are both obtained. The same occurs with respect to the influence of time. Although it does not influence on the efficiency it has a significant influence on residual chromium. A decrease of treatment time shall result on a significant increase of the residual chromium.

8.1.2 Isolation of collagen Biopolymers

Experiments were carried out according to a Box and Hunter Central Rotable and Ortogonal Composite Design for four variables: temperature ($^{\circ}\text{C}$), time (min), concentration of NaOH (M) and H_2O_2 (ml). The influence of the temperature, time, concentration of NaOH, and volume of H_2O_2 on the Bloom degrees was adjusted using a second-order polynomial function. It should be noted that only NaOH concentrations and Temperature were the variables that showed significant influence on the Bloom value.



$$\text{Bloom} = 3444.79 - 8405.46 \cdot [\text{NaOH}] + 12448 \cdot [\text{NaOH}]^2 - 64.18 \cdot T + 0.4937 \cdot T^2$$

Based on the previous results, a second cycle of experiments was designed using the Evolutionary Operation (EVOP) technique in order to reach the optimum. The Two-Level Factorial Plan, in which the experimental plan is based, was centred on this experiment and range of variation of the variables was as follows:

- X1, temperature = 70 – 80 °C
- X2, time = 60 to 90 min
- X3, NaOH concentration = 0.2 M
- C4, H₂O₂ = 1 mL

The excellent bloom values obtained after optimization led to test these isolated biopolymers; either on lab scale or pilot plant, for several industrial applications.

8.1.3 Experiments at Industrial sector

Several types of bioproducts obtained at the optimum zone according to the response surface given by the factorial experimental design described previously on this paper, were used on different industries: Pielcolor S.A., Trumpler española S.A. and Incusa (Spain), Pittards (U.K.), BLC (U.K.) ECCO (The Netherlands).

Biodegradable Films used as Finished in Tanneries

Several pilot-plant trials carried out at this industry in comparing the whole set of casein-based products to biopolymer-based ones. Biopolymer-based compounds showed an excellent binding capacity, good glossy and transparency effect, increasing by mechanic rubbing strong action; good to dry and/or wet rub fastness test, and finally a similar resistance to bleeding out of the ink in function of temperature, time and atmosphere conditioning.

Retanning and Filling Agents

The main target of this hypothesis is to substitute synthetic acrylic, polyurethane resins and protein-based retanning products by the isolated biopolymers.



After the correspondent set of pilot-plant trials it was determined that collagenic biopolymer introduces to leather an important filling effect, similar to the other resins, and raises up the colour intensity of the dyestuffs. Nevertheless when this biopolymer compound is applied alone, the leather produced is rather hard, but when mixing up with fatty acid or some type of triglycerides, its original hardness can be changed to a softer handle.

The current research direction is to copolymerise this bioproduct with a long chain fatty alcohols or acids to give up a permanent soft feeling to the finished leather. However, what is really relevant to mention is that in all trials the colour of dyed leathers were significantly, deeper, stronger and more intense compare to other retanning agents. In addition, the retanning biopolymers have also produced a significant filling effect, thus raising the thickness of treated leathers.

Deliming Agent

Due to the amphoteric nature of these biopolymers, it is possible to use, both as a deliming, or basifying agents. For these special uses the conditions of the controlled hydrolysis of the dechromed collagenic fibres are taken place in stronger hydrolysis conditions, in order to isolate shorter polypeptides chains. When using these biopolymers as deliming agents, the final pH is adjusted with sulphuric acid to 3- 4.5; thus converting the biopolymer into a cationic form, in which the carboxylic groups can mask the calcium already fixed in the skin/hides. This protein biopolymer produces a uniform neutralization of the internal layers of the skin/hides without swelling them, so as happens when strong acids are applied.

Basifying Agent

In a parallel way and adjusting the pH to an alkaline range; such as: 10 – 12 with sodium hydroxide, ammonium hydroxide, sodium carbonate. The optimum results were obtained when these biopolymers are mixed up with oxazolidine, in a proportion of 1:1; thus producing a type of synergy that helps a gradual basifying action during the tanning operation.

Another advantage is that can be added together with the powder chromium(III) basic salts direct to the tanning bath ,without need of a periodical control of the pH and gradual addition of the basifying agent (e.g sodium bicarbonate, etc). After five hours running inside the drum, chromium(III) has completely stabilized the skin/hides in a uniform penetrated layers and producing a high exhaustion of the tanning baths.



8.1.4 Financial Study

According to the economic calculation, the real cost of 1 kg of 30 % solution of biopolymer obtained is of 0.74 \$ or 0.57 €.

8.2 Alternative process for recovery of chromium(III) from tannery effluents

Resin

The resin chosen for the experiments was Amberlite IRA-96 which is an excellent macroporous resin suitable for fixing dichromate and resistant to the reduction reaction in a recycling process. The characteristics of Amberlite IRA-96 are presented in Chapter VI. Nevertheless, it should be pointed out that the maximum temperature allowed by the resin is 90 °C and therefore, the temperature for the reduction must not exceed 90 °C (constraint temperature).

The calculation of fluidization was carried out according to the technical specification of the pilot plant. The results showed that the minimum flow of liquid necessary for fluidization was 77 l·h⁻¹, which is far lower to that available in the pilot plant (3000 l·h⁻¹). Thus, it was expected that the fluidization would be in particles thereby, allowing the resin to exit without any problem through the top of the column. However, on the other hand, it should be noted that the flow was regulated carefully to avoid having an excessively brusque fluidization.

Reducing agents – chromium(III) recovered

The chromium(III) recovered in the ion exchange process is influenced directly by the method used in the reduction-elution stage. The efficiency of the method can be analyzed in function of the chromium(III) recovered, which is determined by the following equation:

$$\text{Recov}_{\text{ratio}} = \frac{(C_{r_{\text{eluted}}} + C_{r_{\text{column depth}}})}{C_{r_{\text{loaded}}}}$$

Where the $C_{r_{\text{eluted}}}$ refers to the Cr^{3+} recovered after the whole process, $C_{r_{\text{column depth}}}$ refers to the Cr^{3+} not fixed in the ionic resin after the loading process and $C_{r_{\text{loaded}}}$ refers to the chromium(VI) content in the tannery-effluent.

The experimental results obtained by the three reducing agents are shown in Table 8.4. All the trials were carried out using the same conditions but using new resin for each test. In the first cycles, the resin retains certain quantity of chromium, but after several cycles, the retention is minimal and the chromium(III) recovered is higher.

Table 8.4: Experimental lab-scale results obtained with the three reducing agents, hydrogen peroxide, sodium bisulphite and glucose

Sample	Cr loaded (mg)	Cr recovered (mg)	Recovered ratio (%)
Hydrogen peroxide			
SAM1	2035	1733	85
SAM2	2131	1706	80
SAM3	1749	1601	92
SAM4	1792	1659	93
SAM5	2013	1776	88
Sodium Bisulphite			
SAM6	1815	1323	73
SAM7	2044	1436	70
SAM8	1985	1484	75
SAM9	1750	1187	68
SAM10	1855	1458	79
Glucose			
SAM11	1712	1205	70
SAM12	1926	1300	67
SAM13	1893	1225	65
SAM14	2176	1551	71
SAM15	1932	1423	74

The Cr^{3+} that was not fixed in the resin after the loading process ($\text{Cr}_{\text{column depth}}$, not shown) was found to be independent to the load (200 to 3000 ml). The concentration of chromium(III) was found to be below 35 ppm for all the experiences. Furthermore, the experiences performed at the pilot plant showed no detectable chromium effluent.

From the three reducing agents, hydrogen peroxide is by far the best reducing agent; the chromium(III) recovered reached around 90 % at laboratory level and 97 % at pilot-plant scale.

8.3 Thermochemical energy storage and conversion: a review of the experimental research under practical conditions

Chapter V gives the summary on the experimental thermal performance of thermal energy storage and conversion systems using thermochemical materials (TCM) under practical conditions.



Most of the research was focused on chemical adsorption processes for refrigeration applications (air conditioning, ice making, deep-freezing, etc.). So far, metal salts with ammonia were the most studied reactants in refrigeration systems (especially chlorides); followed by some metal alloys with hydrogen and few metal salts with water. In the studies using metal salts with ammonia, consolidated composite materials have shown their potential to increase the cooling performance by improving the poor heat and mass transfer of the solid beds (metal salt). Currently, specific cooling powers over 700 W per kilogram of desorbing materials were reached by some ice making prototypes. Nevertheless, recently, Linder *et al.* [1] also obtained a SCP as high as 780 W·kg⁻¹ with a metal hydride air conditioner prototype that used a capillary bundle reactor to increase the heat transfer rate. However, generally, the SCP obtained with the experimental prototypes using metal hydrides is much lower than that obtained with salt ammoniates. Muthukumar and Groll [2] have also pointed out the use of composite materials and advanced cycles concepts as future research lines to increase the efficiency and reduce the cost of these systems.

Unlike the SCP, the reported experimental COP for the current prototypes is still low, usually ranging from 0.2 to 0.65. The thermodynamic cycle operation requires large temperature swings of the sorption reactor during the process which reduces the efficiency (COP) of the system [3,4]. According to Meunier [5] in order to reduce the contribution of a sorption system to the greenhouse effect with respect to compression system, the cooling COP should be at least equal to 1. Although, sorption heat pumps with a COP of less than 1 may be recommended if they use renewable energy sources.

The research on chemical adsorption process and solid-gas chemical reactions for heating applications was less than for cooling applications, and was mainly related to chemical reactions. So far, the reversible hydration and carbonation of metal oxides were the selected reaction for such studies. However, in the past few years, new working pairs appeared for chemical sorption systems. The current research direction is also focused to demonstrate the feasibility of these technologies under practical conditions by improving the heat and mass transfer in the solid bed. So far the specific heating powers of the current systems are in the range from 100 to 300 W·kg⁻¹.

8.3.1 References

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8.4 Characterisation of MgSO₄ Hydrate for Thermochemical Seasonal Heat Storage

Dehydration

The TG analysis indicated that the dehydration of MgSO₄·7H₂O proceed in three steps. The quantitative data from the DSC measurements, literature values for reaction enthalpies, and calculated energy densities are presented in Table 8.5 (heating rate 1 °C·min⁻¹).

Table 8.5: Experimental and theoretical enthalpies of reaction and energy densities for dehydration reactions of magnesium sulphate hydrates

Reaction	T (°C)	ΔH (kJ·mol ⁻¹)			Energy density (GJ·m ⁻³)	
		This study	ref	Abs. Diff	This study	Ref
MgSO ₄ ·7H ₂ O(s) → MgSO ₄ ·6H ₂ O(s) + H ₂ O(g)	25-55	50.2	59.9	19.3	0.3	0.4
MgSO ₄ ·6H ₂ O(s) → MgSO ₄ ·0.1H ₂ O(s) + 5.9H ₂ O(g)	60-265	318.9	340.7	6.8	2.2	2.3
MgSO ₄ ·0.1H ₂ O(s) → MgSO ₄ (s) + 0.1H ₂ O(g)	275	-15.1	6.1	-140.4	-0.1	0.04

The first step occurred at low temperature (25-55 °C) involving a mass loss of 6.9 ± 0.2 % (one water molecule) accompanied by an endothermic process. However, the fact that this transition of MgSO₄·7H₂O to MgSO₄·6H₂O already starts at 25 °C means that when MgSO₄·7H₂O is stored under these conditions, it will (slowly) convert to MgSO₄·6H₂O. This can also be seen in Table 8.5, where the value for the reaction enthalpy is 19.3% lower than the theoretical value, probably due to partial conversion of MgSO₄·7H₂O to MgSO₄·6H₂O prior to the experiments.

Between the first and the second step a melting process occurred at 52.5 °C, which can be a problem for the application of the first dehydration step; melting reduces the bed porosity of the material and thereby the vapour transport through the bed, limiting the ability of the material to take up water again. Further investigation using different heating rate (0.5 °C·min⁻¹, 1 °C·min⁻¹ and .5 °C·min⁻¹), different sample sizes (5 mg, 10 mg, 20 mg, and 50 mg), and different particle distributions (20-38 μm, 38-106 μm, 106-200 μm, and 200-500 μm) revealed that melting can be avoided when using low heating rates (< 1°C), small



particles ($<200 \mu\text{m}$) and/or small sample sizes ($\leq 5 \text{ mg}$). Nevertheless, it should be pointed out that in a heat storage system, which will use large quantities of material, it will be very difficult to meet the criteria.

The second hydration step occurs between $60 \text{ }^\circ\text{C}$ and $265 \text{ }^\circ\text{C}$ involving a total mass loss of $42.2 \pm 0.3 \%$ (5.9 water molecules). From the TG analysis it was observed an initial steep decrease in weight loss signal followed by a more gradual decrease. This suggested that the dehydration of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 0.1\text{H}_2\text{O}$ proceeded in two steps through an $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ intermediate. However, this could not be confirmed by other techniques such as X-ray diffraction. Nevertheless, this first steep decrease in weight loss was accompanied by a sharp endothermic heat flow, both ending at $80\text{--}90 \text{ }^\circ\text{C}$. This indicates that most of the energy is stored below $150 \text{ }^\circ\text{C}$ and therefore, it means that approximately $2.2 \text{ GJ}\cdot\text{m}^{-3}$ can be stored when heating $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ to $150 \text{ }^\circ\text{C}$.

Finally, the in last dehydration step involves the mass loss of $0.5 \pm 0.1 \%$ and is accompanied by an exothermic process. According to Ruiz-Agudo *et al.* (Ref) the exothermic process is a result of a recrystallization from an amorphous precursor to crystalline MgSO_4 . This last observation was further confirmed by X-ray powder diffraction, in which the diffraction patterns for temperatures between $80 \text{ }^\circ\text{C}$ and $276 \text{ }^\circ\text{C}$ showed that in this temperature range and amorphous phase of formed, which converts to crystalline MgSO_4 .

Hydration - Influence water vapour pressure

The influence of the partial water pressure on the hydration behaviour was studied using a thermal analysis at $25 \text{ }^\circ\text{C}$, and at partial water pressure of 1.3 kPa and 2.1 kPa . The results revealed that at $25 \text{ }^\circ\text{C}$ an increase in water vapour pressure from 1.3 kPa to 2.1 kPa results in improved water uptake; six water molecules instead of one molecule are taken up per MgSO_4 molecule. The single step transformation from MgSO_4 to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ has an energy density of $1.8 \pm 0.1 \text{ GJ}\cdot\text{m}^{-3}$, which is approximately 88% of the energy density of the corresponding dehydration reaction ($2.1 \pm 0.1 \text{ GJ}\cdot\text{m}^{-3}$).

Hydration - Influence temperature

The effect of increasing the temperature from $25 \text{ }^\circ\text{C}$ to $50 \text{ }^\circ\text{C}$ on the hydration was studied with a constant partial water vapour pressure of 2.1 kPa . The results indicated that at $50 \text{ }^\circ\text{C}$ and 2.1 kPa (pH_2O) the material is unable to take up water.



Hydration - Influence of the particle size and layer thickness

Furthermore, the influence of the particle size and layer thickness on the water uptake was also studied. The experiments were performed at 25 °C and partial water pressure of 2.3 kPa. The results indicated that the variation in the particle size distribution has a very limited effect on the hydration, since the water uptake for all studied particle size distribution corresponded to six water molecules. On the other hand, the hydration was strongly affected by a change in the layer thickness; since the hydration process is completed in a shorter time for smaller layer thickness. Therefore, the vapour transport through the layer thickness is a limiting factor in the hydration process.

The effect of dehydration and hydration on grains

The effect of the dehydration and hydration on grains size was studied by scanning electron microscopy (SEM) for a particle size distribution of 38-106 µm. The material (40 g) was dehydrated to 150 °C with 1 °C·min⁻¹ inside an oven and hydrated for 20 h inside a climate room at 20 °C and RH=52 %, corresponding to p_{H₂O}=1.2 kPa. After dehydration, the particle size was reduced and a fraction of small particles were formed (~1-10 µm). Apparently the formation of new cracks and pores is so violent that smaller particles are expelled during the dehydration. The formation of small particles during the dehydration can be a problem for a future TCM reactor; for instance when a fluidized bed is used. On the other hand, after hydration, the particle size distribution was almost not affected: a small shift to larger particles was observed.

Hydration – Effect total system pressure

Finally, a separated experiment was performed in a closed system using a fixed bed reactor which is connected to an evaporator/condenser. The system was evacuated to 2.8 mbar using a vacuum pump system in order to promote the diffusion of water vapour to the salt hydrate. After dehydration of MgSO₄·7H₂O to 150 °C in an oven, the material was hydrated at 50 °C and 1.3 kPa. A maximum temperature increase of 4°C was measured in the reactor during the hydration which indicates that under low-pressure magnesium sulphate reacts with water producing enough heat to create this small temperature lift.

8.5 Characterisation of salt hydrates for compact thermochemical storage

In this work, salts of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were evaluated experimentally as potential TCM. The salts hydrates were first dehydrated in an oven to $150\text{ }^\circ\text{C}$ at $1\text{ }^\circ\text{C} \cdot \text{m}^{-1}$ and then hydrated using a closed fixed-bed reactor operating at low pressure under two conditions; as shown in Table 8.6.

Table 8.6: Experimental conditions during hydration experiments.

	Reactor		Evaporator
	Temperature ($^\circ\text{C}$)	Temperature ($^\circ\text{C}$)	water vapour pressure (kPa)
I	25	25	3.2
II	50	10	1.3

The temperature increase measured inside the fixed-bed reactor during the hydration process was used to evaluate each salt hydrate.

Table 8.7 shows the maximum temperature increase measured inside the fixed-bed reactor, after the hydration process under the two condition, I and II (Table 8.6)

Table 8.7 Maximum temperature increase measured for the four salts hydrates. Under experimental conditions I (at $25\text{ }^\circ\text{C}$ and 2.1 kPa) and II (at $50\text{ }^\circ\text{C}$ and 1.3 kPa)

Experimental Conditions	Temperature lift ($^\circ\text{C}$)	
	I	II
$\text{MgSO}_4 \cdot \text{H}_2\text{O}(\text{s})$	6	4
$\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}(\text{s})$	10	1
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$	63	19
$\text{CaCl}_2(\text{s})$	62	11

The results indicate that all salts are able to release the stored heat during hydration, even under practical conditions (II, TCM seasonal solar heat storage). The temperature increase of the bed measured during the hydration was found to be dependent on the type of salt; under identical conditions (II), the chlorides showed a larger temperature lift than the sulphates. However, it was found that the chlorides tend to overhydrate transforming to a sol-gel like structure (deliquescence). This is an undesirable effect since it reduces the bed porosity of the material and the ability to take up water again.



9 Conclusions

9.1 Transformation plant for converting chromium(III) waste into chemical products for the leather industry

- Complete elimination of physical volume occupied by these types of chromium(III) collagen wastes (99% of removal) has been shown: thus a tremendous environmental problem has been solved; and, consequently a considerable reduction in the management cost of such a waste has been gained.
- The new dechroming process based on the oxidation with peroxides in alkaline medium, followed by washes, reduces the chromium(III) content from 50,000 ppm original collagen waste to 20-90 ppm (on dry weight basis of collagen wastes).
- Recovery and reuse of the chromium(III) present in chromium(III)-tanned wastes was demonstrated. The chromium(VI) produced with this process is reduced with hydrogen peroxide in acidic medium back to chromium(III) inside of a storage stainless steel stirred tank (high speed kinetic reaction). Finally, adjustment of its basicity to 33° Sch. followed by addition of the necessary amount of solid basic chromium(III) powder salts prepares this bath to the appropriate chromium(III) concentration to be reused into a conventional industrial tanning process.
- Isolation of industrially reusable bioproducts in tanneries was shown. Once the majority of chromium(III) was separated from the original chromium(III)-collagen wastes different types of bioproducts could be obtained. Thus, a range of the following chemical leather tannery products were reproduced: retanning and filling agents, biodegradable film in the finishing operation of certain glazing leathers and delimiting and basifying agents.
- In addition, the process for obtaining collagenic biopolymers out of chromium(III)-tanned wastes can be tailored made for each tannery; therefore diminishing the transport cost from an external communal plant that could treat wastes from different tanneries. According to the economic calculation described in the above Potential Exploitation section, the real cost of 1 kg of 30 % solution of biopolymer obtained is of 0.74 \$ or 0.57 €.



- A major use of these biopolymers is as retaining/filling agents in tanneries. Main physical-mechanical properties (tensile strength, tear load, lastometer, etc.) have been shown to be either equal, or even higher values, in comparison to the majority of other protein-based retaining products.
- This present project has introduced a few novelties with respect to previous studied processes. These include: a) grinding the chromium(III)-tanned wastes to a diameter of 1 mm to 5 mm, b) partial retanning of chromium(III)-wastes with formaldehyde to stabilize them, mainly in alkaline medium, so neutral salts can be eliminated; therefore, lowering the residual salt content of the effluents and obtaining better quality of the biopolymers, c) completely elimination of the ion-exchange unit to separate the chromium(VI), showing a great saving for the global installation, d) the authors recommend achieving a 30 % solution of biopolymers rather than adding a spray drier unit, which in turn is a significantly equipment cost savings.

9.2 Alternative process for recovery of chromium(III) from tannery effluents

- A process to recover tannery-chromium(III) from tannery effluents, alternative to the conventional precipitation one. This process is based on the oxidation of chromium(III) to chromium(VI), followed by two sequential steps; a) fixation into a ion-exchange resin and, b) reduction to chromium(III) in a batch combined system.
- Several oxidation methods have been assayed, in order to improve the final results obtained with hydrogen peroxide. An oxidation with air could be a previous stage to the hydrogen peroxide in order to oxidize part of the organic matter present in the sample.
- The oxidation reaction of chromium(III) to chromium(VI) takes place by the action of hydrogen peroxide in an alkaline medium, such as, sodium carbonate, which has proved to be the best.
- In different experiences, both laboratory level and pilot plant scale, the outlet of the column has given no detectable chromium (less than 0.5 ppm).
- In the reduction stage, three different kinds of reducing agents were used, acid hydrogen peroxide, sodium bisulphite and glucose; the first being by far the best. It is important to mention that this operation is a complete novelty with respect to the previous process where the reduction



took place *in situ*, inside the column; nevertheless, in this new process the ion-exchange resin-dichromate bound is conveyed to a reactor vessel, where the reduction is carried out with better temperature control. At the end of the reduction, washes, etc., the resin will be adjusted to the proper pH and poured into the column to start a new cycle.

- An excellent chromium(III) recovered ratio has been achieved using the different reducing agents; emphasizing that the chromium(III) recovered using hydrogen peroxide has reached around 97 % recovery.
- The recovered concentrated solution of chromium(III) was basified to 33 °Sch basicity, with addition of sodium sulphate, then the liquor could be used into the traditional tanning operation. This recovered basified chromium(III) liquor produces a clear, uniform light blue colour of the grain surface, thus allowing finishing in all the range of light colours.
- A thorough economic study is ongoing, in order to compare the cost of both processes; a) precipitation with magnesium and/or calcium oxides, and b) with the present proposal. It is fundamental to underline that the commercial ion exchange resin can be recycled, at least 40 times; therefore, diminishing significantly the cost of this product and the whole process.

9.3 Thermochemical energy storage and conversion: a review of the experimental research under practical conditions.

This work presents a review of the current experimental research on chemical adsorption process and chemical reactions based on solid-gas systems for thermal energy storage and conversion. Chapter V gives a summary of the experimental thermal performances under practical conditions obtained by the different prototypes built over the last two decades.

Refrigeration technologies based on metal salts and ammonia has progressed considerably over the last twenty years. Consolidated composite materials have shown their potential to increase the cooling performance and currently, specific cooling powers over 700 W per kilogram of desorbing materials were reached by some ice making prototypes.



Recently, Linder *et al.* [1] also obtained a SCP as high as $780 \text{ W}\cdot\text{kg}^{-1}$ with a metal hydride air conditioner prototype that used a capillary bundle reactor to increase the heat transfer rate. However, generally, the SCP obtained with the experimental prototypes using metal hydrides is much lower than that obtained with salt ammoniates. Muthukumar and Groll [2] have also pointed out the use of composite materials and advanced cycles concepts as future research lines to increase the efficiency and reduce the cost of these systems.

By contrast, the reported experimental COP for the current prototypes is still low, usually ranging from 0.2 to 0.65. According to Meunier [3] in order to reduce the contribution of a sorption system to the greenhouse effect with respect to compression system, the cooling COP should be at least equal to 1. Although, sorption heat pumps with a COP of less than 1 may be recommended if they use renewable energy sources.

The research on chemical sorption process and chemical reactions for heating applications was less than for cooling applications, and was mainly related to chemical reactions. However, in the past few years, new working pairs appeared for chemical sorption systems. The current research direction is also focused to demonstrate the feasibility of these technologies under practical conditions by improving the heat and mass transfer in the solid bed. So far the specific heating powers of the current systems are in the range from 100 to $300 \text{ W}\cdot\text{kg}^{-1}$.

Therefore, the main research direction for future research can be summarized in the following points:

- Although researchers obtained promising experimental results with consolidated composite materials, improvements on heat transfer often results in a deployment of mass transfer [4,5]. In cases of low operating vapour pressures (water, methanol), the reactor requires of a short mass transfer path (thickness) and large number of mass transfer channels which reduces power output per volume of reactor [5-7]. Therefore, research efforts are needed towards developing advanced composite materials with good heat and mass transfer and development of advanced designs and configuration for reactor and heat exchanger.
- Testing and developing advanced cycles designs to improve the COP, towards 1 or further. In addition, cascading cycles can be used to improve the efficiency of the current commercial absorption devices. The chemical sorption or reaction heat pump is used as the topping cycle as it can be driven at higher temperature than the absorption devices.



- Perform long-duration test to study the durability and stability of the material. According to Wang *et al.* [8] problems of expansion, decomposition, deterioration and corrosion in the chlorides salts-ammonia systems are the main drawback for its widespread utilization
- Built and test larger scale prototypes (more modules or larger reactors) to prove the same SCP or SHP and COP as with the current prototypes (small-scale).
- Intensification of the experimental research on chemical sorption process and chemical reaction systems for heating applications as the scope for its application is very wide, especially for chemical reactions. The potential of chemical reaction heat pump systems lies on the fact that they work at very high temperatures which no other commercial heat pump can reach.
- Although, the research for short or long term thermal storage is in the early stage, only few experiments have been carried out for short discharging periods. More experiments are required to demonstrate the feasibility for short and long term heat storage.
- Finally, another important point for its application is that these technologies are operated under a variable waste heat temperature. Therefore, a control strategy of these systems should be optimized in order to obtain a high efficiency [9].

Although much more research efforts are needed to bring these technologies to the market, the advanced technology development have been reflected on the experimental results.

9.3.1 References

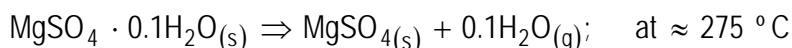
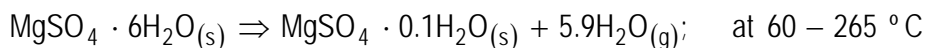
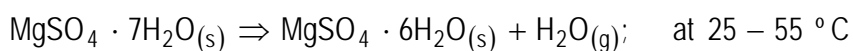
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9.4 Characterisation of MgSO₄ Hydrate for Thermochemical Seasonal Heat Storage

- Magnesium sulphate heptahydrate (MgSO₄·7H₂O) was investigated as potential material for compact seasonal heat storage. The results showed that the dehydration of MgSO₄·7H₂O proceeds in at least three steps:



- The second dehydration step has a high-energy density ($2.2 \pm 0.1 \text{ GJ}\cdot\text{m}^{-3}$), the reaction primarily occurs in a temperature range that can be covered by medium temperature collectors ($\leq 150 \text{ }^\circ\text{C}$), and problems with melting of the MgSO₄·7H₂O can be avoided. Therefore, this step is the most interesting for compact seasonal solar heat storage.
- Experiments indicate that the second dehydration step involves several consecutive dehydration steps, probably including a MgSO₄·2H₂O intermediate, but it was not possible to clearly identify each individual step. X-ray diffraction experiments indicated that the second dehydration step involves a material structure change from crystalline (MgSO₄·6H₂O) to an amorphous phase until crystalline MgSO₄ is formed.
- Hydration experiments performed at atmospheric pressure reveal that the amount of water taken up by MgSO₄ depends on partial water vapour pressure and temperature. Experiments reveal that at 25 °C an increase in water vapour pressure from 1.3 kPa to 2.1 kPa results in improved water uptake: Six water molecules instead of one molecule are taken up per MgSO₄ molecule. The single step transformation from MgSO₄ to MgSO₄·6H₂O has an energy density of 1.8 0.1

$\text{GJ}\cdot\text{m}^{-3}$, which is approximately 88 % of the energy density of the corresponding dehydration reaction ($2.1 \pm 0.1 \text{ GJ}\cdot\text{m}^{-3}$).

- Increasing the temperature from 25 °C to 50 °C at constant $p_{\text{H}_2\text{O}} = 2.1 \text{ kPa}$ results in a strongly reduced water uptake by MgSO_4 . It means that under practical conditions (partial water vapour pressure of 1.3 kPa and $T > 40 \text{ °C}$), the material is not able to take up water at atmospheric pressure.
- However, an initial test using a closed fixed-bed reactor operating at low pressure showed a maximum temperature increase of 4 °C. This result indicates that under low-pressure conditions dehydrated material is able to react with water under practical conditions.

9.5 Characterisation of salt hydrates for compact thermochemical storage

- The temperature lift of the bed measured during the hydration was found to be dependent on the type of salt; under identical conditions, the chlorides (calcium chloride and magnesium chloride) show a larger temperature lift ($\Delta T = 11\text{-}19 \text{ °C}$) than the two sulphates (aluminium sulphate and magnesium sulphate, $\Delta T = 1\text{-}4 \text{ °C}$).
- Under practical conditions, the chlorides can deliver heat to the residential heating system at a higher temperature than the sulphates. Nevertheless, it should be pointed out that, due to the highly hygroscopic nature of the chlorides, these materials tend to overhydrate transforming to a sol-gel like structure (deliquescence), which is an undesirable effect since it reduces the bed porosity of the material and the ability to take up water again. Therefore, this problem needs to be solved before using chlorides as TCM for compact seasonal heat storage.
- Finally, once the aforementioned problem is solved, it is recommended to use magnesium chloride as TCM for compact seasonal heat storage in the built environment.



9.6 General Conclusions

The current thesis presents a thorough and extensive work to move towards a more energy and resource efficient economy by means of chemical reactions. In particular, the main contributions of chemistry and chemical engineering to sustainability are:

1. The oxidation of chromium (III) to chromium(VI) using hydrogen peroxide in alkaline medium shows to be a quick and effective procedure for dechroming of collagenic tanned wastes with the following advantages:
 - ✓ The isolation of high added value collagenic biopolymers from chromium(III) solid tanned wastes allows to re-use a solid-waste that otherwise are generally processed for disposal or land application.
 - ✓ Solve an important environmental problem faced by the leather industry, which incurs significant costs in managing this type of wastes; especially, because under the current European legislation the accumulation in otherwise approved dumps of waste materials containing chromium(III) is forbidden.
 - ✓ Gain financial benefits from obtaining industrially re-usable bioproducts .
 - ✓ The reduction of chromium(VI) back to chromium(III) using hydrogen peroxide in acid medium (sodium bisulphite or cellulose) allows to recovery and re-use of the chromium(III) present in chromium(III) tanned wastes solid
2. The same oxidation-reduction reaction is used for recovery of the chromium(III) from the tannery effluents. Additionally, the novel process allows to recover chromium(III) more purified, in a quicker way and with lower energy consumption than the conventional alkaline precipitation method.
3. The complete review on thermochemical energy storage technologies reveals that a wide range of reversible thermochemical reactions (solid-gas) can be exploited, on the one hand, for converting waste heat into usable energy from industrial process, power plants, combustion engines and, on the other hand, to bridge the gap between energy supply and demand, especially important for increasing the potential of renewable energies due to seasonal and daily changes.



4. Furthermore, the review shows an important progress towards commercialization for a wide range of cooling and heating applications which would result in a substantial energy savings and a reduction in CO₂ emission. Additionally, TES can contribute to potentiate the use of solar energy (quicker implementation) and thus, to the shift from non-renewable energy source to renewable energy source.

5. In this thesis, a seasonal solar heat storage system for low energy buildings was proposed using the salt hydrates of MgSO₄·7H₂O, Al₂(SO₄)₃·18H₂O, CaCl₂·2H₂O and MgCl₂·6H₂O as a new way for storing solar heat. The experimental characterisation reveals that MgCl₂·6H₂O could be a promising material if problems with deliquescence are solved. In this sense, the material would enable to store the excess of solar supply during the summer and used to cover the space heating demand during the less sunny periods in winter. Therefore, the TCM system would allow to cover the annual space heating demand of a low energy building by means of solar energy.

