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GREEN INNOVATIONS IN FLOTATION, PROTEIN SEPARATION, FLUE GAS REUSE, NEW PROCESS SYSTEMS, SULFIDE PRECIPITATION, CHROMIUM REMOVAL, AND TANNERY WASTE TREATMENT

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ABSTRACT

This publication reviews the technical information from UNIDO, USEPA and LIWT, and covers the following subjects concerning the leather tanning industry: industry description, subcategories, tannery operations, pollutants, effluent discharge limitations, Best Practical Control Technology Achievable (BPCTA), Best Available Technology Economically Achievable (BATEA), current waste treatment systems, environmental problems, process improvements, new process equipment, innovative process systems, independent PC WW Treatment System, DAF, DAFF, combined DAF-DAFF, dissolved protein analysis and removal, BPCTA and BATEA examples, dissolved carbon dioxide flotation (DCDF), carbonation, flue gas recycle, GHG reduction, ferrous sulfide precipitation process for removing toxic sulfides, ferrous sulfide sludge recycle for removing toxic chromium (III) , physicochemical sequencing batch reactor (PC-SBR); biological flotation aerobic-anoxic contact stabilization process, membrane biological flotation reactor (MFBR), tannery discharge limitations, and glossary. This publication is one of the authors' memoirs. The researchers around the world are invited to investigate the green innovations explored by LIWT for further improvement.

KEYWORDS: Memoir, New R&D Leather Tanning industry, wastewater treatment, United Nations Industrial Development Organization (UNIDO), USEPA, Lenox Institute of Water Technology (LIWT), Krofta Engineering Corporation (KEC), Best Available Technology (BAT), Best Practical Control Technology Achievable (BPCTA), Best Available Technology Economically Achievable (BATEA), Dissolved air flotation (DAF), DAF-filtration (DAFF), Dissolved carbon dioxide flotation (DCDF), Carbonation, Protein analysis, Waste flue gas recycle for protein removal, Greenhouse gas reduction, Ferrous sulfate for chemical precipitation of sulfide ions, Reuse of ferrous sulfide waste sludge for ion exchange removal

of chromium (III) ions, Vacuum filtration, Sustainable tannery wastewater treatment examples, Glossary, Supracell DAF, Sandfloat DAFF, Sedifloat, AquaDAF, Clari-DAF, Combined DAF-DAFF, KAMET, Independent physicochemical wastewater treatment system (IPCWWTS), Biological flotation aerobic-anoxic contact stabilization, Physicochemical sequencing batch reactor (PC-SBR), Membrane biological flotation reactor (MBFR).

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ACRONYM

BAT: Best Available Technology.

BATEA: Best Available Technology Economically Available.

BOD: Biochemical oxygen demand.

BPCTA: Best Practical Control Technology Available.

COD: Chemical oxygen demand.

DAF: Dissolved air flotation.

DAF-DAFF: DAF and DAFF package plant.

DAFF: Dissolved air flotation and filtration.

DAOF: Dissolved air-ozone flotation.

DCDF: Dissolved carbon dioxide flotation.

DCDF: Dissolved carbon dioxide flotation.

DNF: Dissolved nitrogen flotation.

DOF: Dissolved oxygen flotation.

DOF: Dissolved ozone flotation.

GAC: Granular activated carbon.

GHG: Greenhouse gas.

gpd: Gallon per day.

IPCWWTS: Independent physicochemical wastewater treatment system.

KAMET: Krofta Advanced Municipal Effluent Treatment.

KAMWT: Krofta Advanced Municipal Water Treatment.

KEC: Krofta Engineering Corporation.

LIWT: Lenox Institute of Water Technology.

MBFR: Membrane biological flotation reactor

MBR: Membrane bioreactor.

MDL: Method detection limit.

MGD: Million gallons per day.

O&G: Oil and grease.

O&M: Operation and maintenance.

PAC: Powdered activated carbon.

PC-SBR: Physicochemical sequencing batch reactor

PSES: Pretreatment Standards of Existing Sources.

PSNS: Pretreatment Standards of New Sources.

R&D: Research and development.

RBC: Rotating biological contactor.

TDS: Total dissolved solids.

TKN: Total Kjeldahl nitrogen.

TSS: Total suspended solids.

UNIDO: United Nations Industrial Development Organization.

USEPA: US Environmental Protection Agency.

1. LEATHER TANNING INDUSTRY

1.1 Introduction

1.1.1 General Tanning Industry Description

Leather tanning or finishing is the conversion of animal hides or skins into leather. So leather tanning is a general term for the numerous processing steps involved in converting animal skins or hides into leather. Cattlehides, sheepskins, and pigskins are the major hides and skins used most often to manufacture leather.. To a lesser extent, hides and skins of horses, goats, deer, elk, calves, and other animals are also tanned. Cattlehide or cattle-like hide have short hair and are relatively heavy. Deerskin, horsehide, cow bellies, splits (flesh side of tanned hides which is usually processed separately into suede types of leather) and hides of a similar nature are included in this group. Sheep or sheep-like skins have long hair and are relatively light. Goatskin and other similar hides are included in this group. Pig or pig-like skins have short hair or are hairless and are relatively light. This group includes skins which have little hair, yet typically require unhairing operations. The type of raw material (hides or skins) and the amount of processing already performed on the raw materials received by the facility determines the type of processes necessary to produce finished or partially processed leather. [1-4]

It is important to note that it is the inner layer of an animal skin, which consists primarily of the protein collagen, that is made into leather. Tanning is the reaction of the collagen fibers with tannins, chromium, alum, or other tanning agents to help stabilize or preserve the skin to make it useful.

Tanneries purchase hides and skins to manufacture leather for shoes, garments, upholstery, luggage, gloves, handbags, sporting goods, and a variety of other products.

There are three major hide and skin types used to manufacture leather are cattle-hides, sheepskins, and pigskins. Cattle-hides constitute the bulk of the tanning performed in the U.S., representing about 90 percent of the total estimated weight of hides tanned. There are three major leather manufacturing steps: (a) beam-house operations which wash and soak the hides or skins and remove the attached hair; (b) tan-yard processes in which the tanning agent reacts with and stabilizes the proteinaceous matter in the hides or skins, and (c) re-tanning and wet finishing processes which accomplish further tanning by chemical agents such as dyes, lubricants, and various finishes.

The major pollutants from the leather tanning industry are: (a) conventional pollutants, such as, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), pH and oil and grease (O&G); (b) non-conventional pollutants, such as ammonia, total Kjeldahl nitrogen (TKN), nitrate and sulfide; and (c) toxic pollutants, such as, 2,4,6 trichlorophenol, chloroform, 1,2 dichlorobenzene, 1,4 dichlorobenzene, ethylbenzene, methylene chloride (dichloromethane), naphthalene, pentachlorophenol, phenol, bis-(2-ethyihexyl) phthalate, toluene, heavy metals (chromium, copper, lead, nickel & zinc), and cyanide.

1.1.2. Publication Objectives

This publication initially reviews the technical information from the United Nations Industrial Development Organization (UNIDO), the US Environmental Protection Agency (USEPA) and the Lenox Institute of Water Technology (LIWT) [3-7]. Subsequently the LIWT research and developments (R&D) accomplishments in tannery waste treatment are introduced. The researchers around the world are invited to investigate the green innovations explored by the LIWT for further improvement.

1.1.3 Publication Coverage

The coverage of this publication includes: (a) leather tanning industry description, major hide and skin types and standard leather manufacturing steps; (b) tannery operations; (c) conventional, non-conventional and toxic pollutants in the leather tanning industry wastewater; (d) the Best Available Technology (BAT), the Best Practical Control Technology Achievable (BPCTA), and the Best Available Technology Economically Achievable (BATEA); (e) the BPCTA and BATEA currently applied to tannery waste treatment; (f) the problems of existing environmental technologies (BPCTA and BATEA) for tannery waste treatment; (g) process improvements accomplished by replacing conventional sedimentation and filtration with innovative dissolved air flotation (DAF) and DAF-filtration (DAFF); (h) advanced DAF and DAFF process equipment commercially available; (i) conventional biological secondary treatment versus innovative physicochemical (PC) secondary treatment; (j) an example: BPCTA for tannery waste treatment using Supracell DAF and Sandfloat (DAFF) as PC secondary treatment; (k) an example: BATEA for tannery waste treatment using Supracell DAF, biological secondary treatment and DAFF tertiary treatment; (l) advantages of new BPCTA and BATEA for future tannery waste treatment; (m) leather tanning industry nine subcategories; (n) technology schematic systems for treating wastes from various sub-categorizations; (o) innovative dissolved carbon dioxide flotation (DCDF) and vacuum filtration; (p) innovative waste flue gas (carbon dioxide) recycle for protein removal by carbonation; (q) innovative chemical precipitation process for removal of toxic sulfide ions from tannery beamhouse waste using ferrous sulfate; (r) innovative ion exchange process for removing toxic chromium (III) ions from tannery tanyard wastewater by reusing ferrous sulfide waste sludge; (s) independent physicochemical wastewater treatment system (IPCWWTS) and physicochemical sequencing batch reactor (PC-SBR); (t) biological flotation aerobic-anoxic contact stabilization process, (u) membrane biological flotation reactor; (v) tannery discharge limitations, and (w) glossary of tannery waste treatment. This publication is timely written for celebration of the 2022 Earth Day (April 22, 2022) and is one of the authors' memoirs. [6-22]

1.1.4 Sustainable Industrial Development

Best practicable control technology currently achievable (BPCTA, or BPT) is a technology acceptable by the government taking into account such factors as age of equipment, facilities involved, process employed and process changes, engineering aspects of control techniques, and environmental impact apart from water quality, including energy requirements. In assessing BPT for a particular category of industry, a balance is struck between total cost and effluent reduction benefits. BPT is a treatment required by July 1, 1977 in the USA for industrial discharge to surface waters as defined by Section 301 (b)(1)(A) of the PL92-500.

Best available technology economically achievable (BATEA, or BAT) is the highest degree of technology proved to be designable for plant-scale operation so that costs for this treatment may be higher than for treatment by best practicable technology (BPT), but economically achievable. BATEA, or BAT, is the treatment required by July 1, 1983 in the USA for industrial discharge to surface waters as defined by Section 301 (b)(2)(A) of the PL92-500.

For most of the developing countries, achievement of at least BPCTA, or BPT may be their industrial development goal. All industrial countries should aim at achieving the highest degree of technology, BATEA or BAT. This publication covers both BPCTA and BATEA for reference by all industrial developers. The step-by-step investigations may lead to a sustainable final waste management solution. This methodologies may be applied to not only for the leather tanning industry, but to all industries.

1.2 Beamhouse Operations

There are three major groups of subprocesses required to make finished leather: Beamhouse operations; tanyard processes; and retanning and finishing processes. These processes and types of wastewater generated are described in the following sections.

The beamhouse operations shown in Figure 1 consist of four typical subprocesses: (a) side and trim; (b) soak and wash; (c) fleshing; and (d) unhairing. Side and trim is the cutting of the hide into two sides and trimming of areas which do not produce good leather. In soak and wash processes, the hides or sides are soaked in water for eight to twenty hours to restore the moisture that was lost during curing. Washing removes dirt, salt, blood, manure, and nonfibrous proteins. [2-3]

Fleshing is a mechanical operation which removes excess flesh, fat, and muscle from the interior of the hides. Cold water is used to keep the fat congealed. The removed matter is normally recovered and sold for conversion to glue. Unhairing involves using calcium hydroxide, sodium sulfhydrate, and sodium sulfide to destroy the hair (hair pulp) or remove hair roots (hair save), loosen the epidermis, and remove certain soluble skin proteins. A mechanical. unhairing machine is used to remove hair loosened by chemicals in the hair save process. .

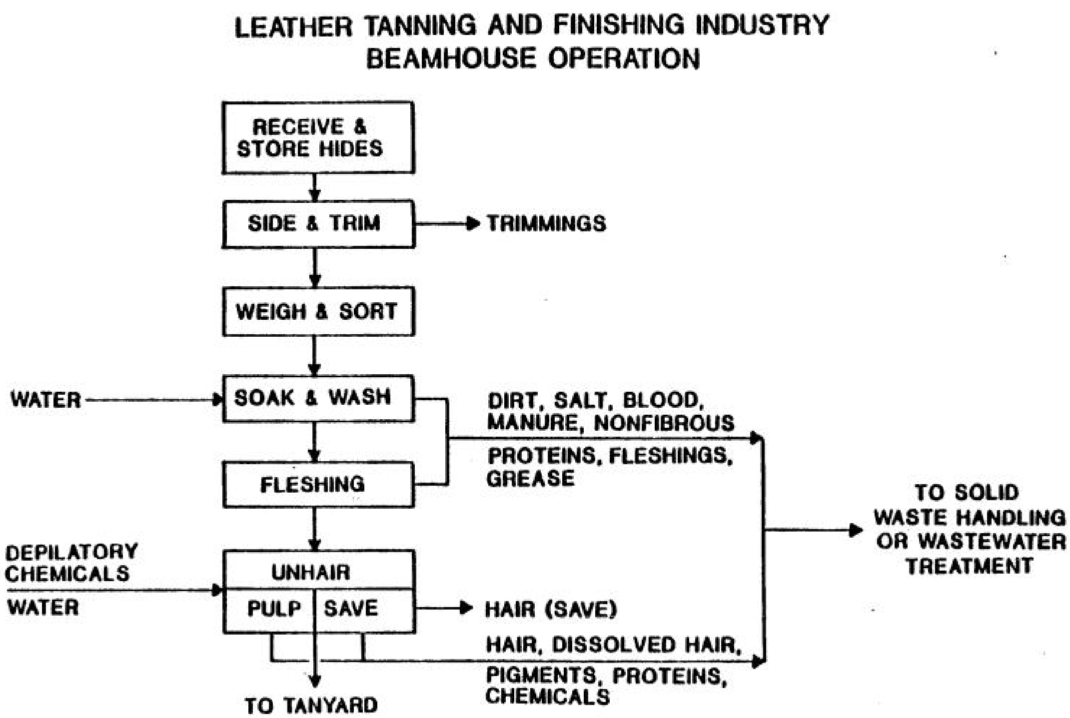

Figure 1. Beamhouse Operations (Source: USEPA)

1.3. Tanyard Processes

They follow the beamhouse operations and consist of (a) bating, (b) pickling, (c) tanning, (d) wringing, (e) splitting, and (f) shaving, shown in Figure 2.

Bating involves the addition of salts of ammonium sulfate or ammonium chloride used to convert the residual alkaline chemicals present from the unhairing process into soluble compounds which can be washed from the hides or skins. The addition of bates, enzymes similar to those found in the digestive systems of animals facilitate the separation of the collagen protein fibers and destroy most of the remaining undesirable constituents of the hide, such as hair roots and pigments.

Pickling prepares the hides to accept the tanning agents (i.e., chrome) usually by adding sulfuric acid to provide the acid environment necessary for chromium tanning. In the tanning process, tanning agents such as trivalent chromium, vegetable tannins, alum, syntans, formaldehyde, gluteraldehyde, and heavy oils, convert the raw collagen fibers of the hide into a stable product no' longer susceptible to putrefaction or decomposition. They also improve the dimensional stability, resistance to heat, chemicals and abrasion, and flexibility of the raw materials.

Vegetable tanning is used in the production of heavy leathers such as sole leather and saddle leather. Chromium tanning is usually preferred by the majority of leather users, i.e., shoe and garment manufacturers.

Blue hides (hides after beamhouse and tanyard operations) are wrung to remove excess moisture through a machine similar to a clothes wringer.

Splitting adjusts the thickness of the tanned hide to the requirements of the finished product and produces a split ("drop") from the flesh side of the hide. These splits may or may not be retanned and wet finished at the same facility.

Shaving removes any remaining fleshy matter from the flesh portion of the hide, as shown in Figure 2.

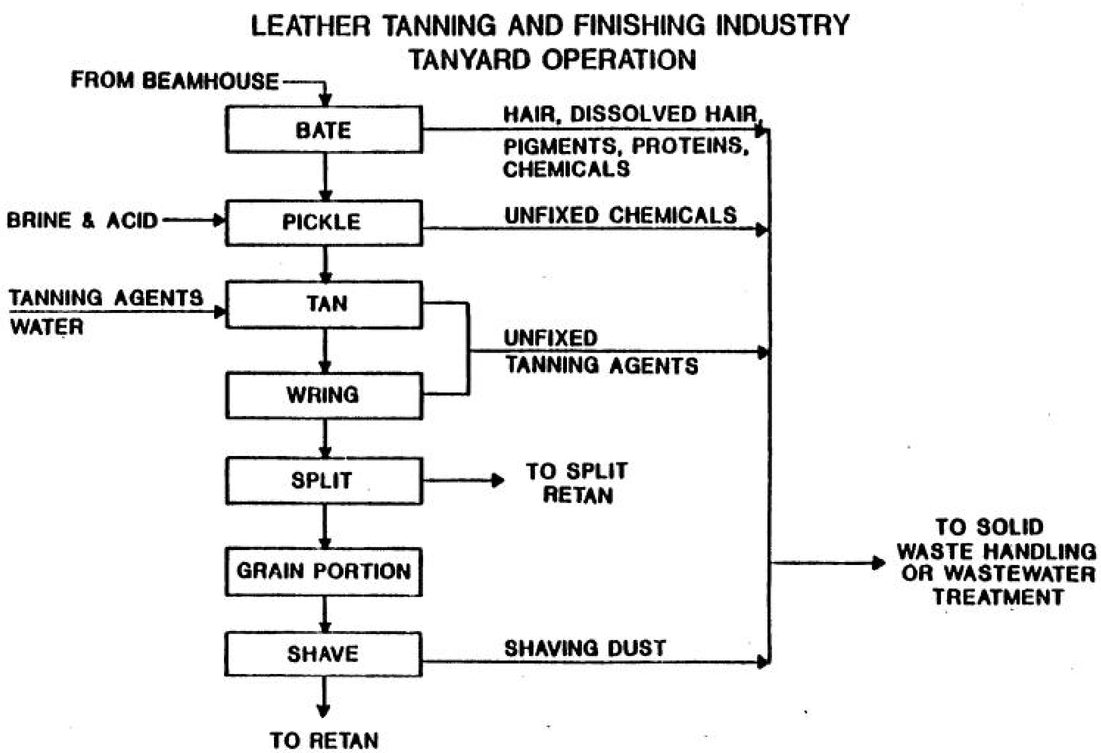

Figure 2. Tanyard Operation (Source: USEPA)

1.4. Retanning and Wet Finishing Processes

These are the final process steps after beamhouse operations and tanyard processes that give the tanned hide special desired characteristics. The final process steps used include: (a) retanning, (b) bleaching, (c) coloring, and fatliquoring, and (d) finishing. Figure 3 shows the retanning and wet finishing processes.

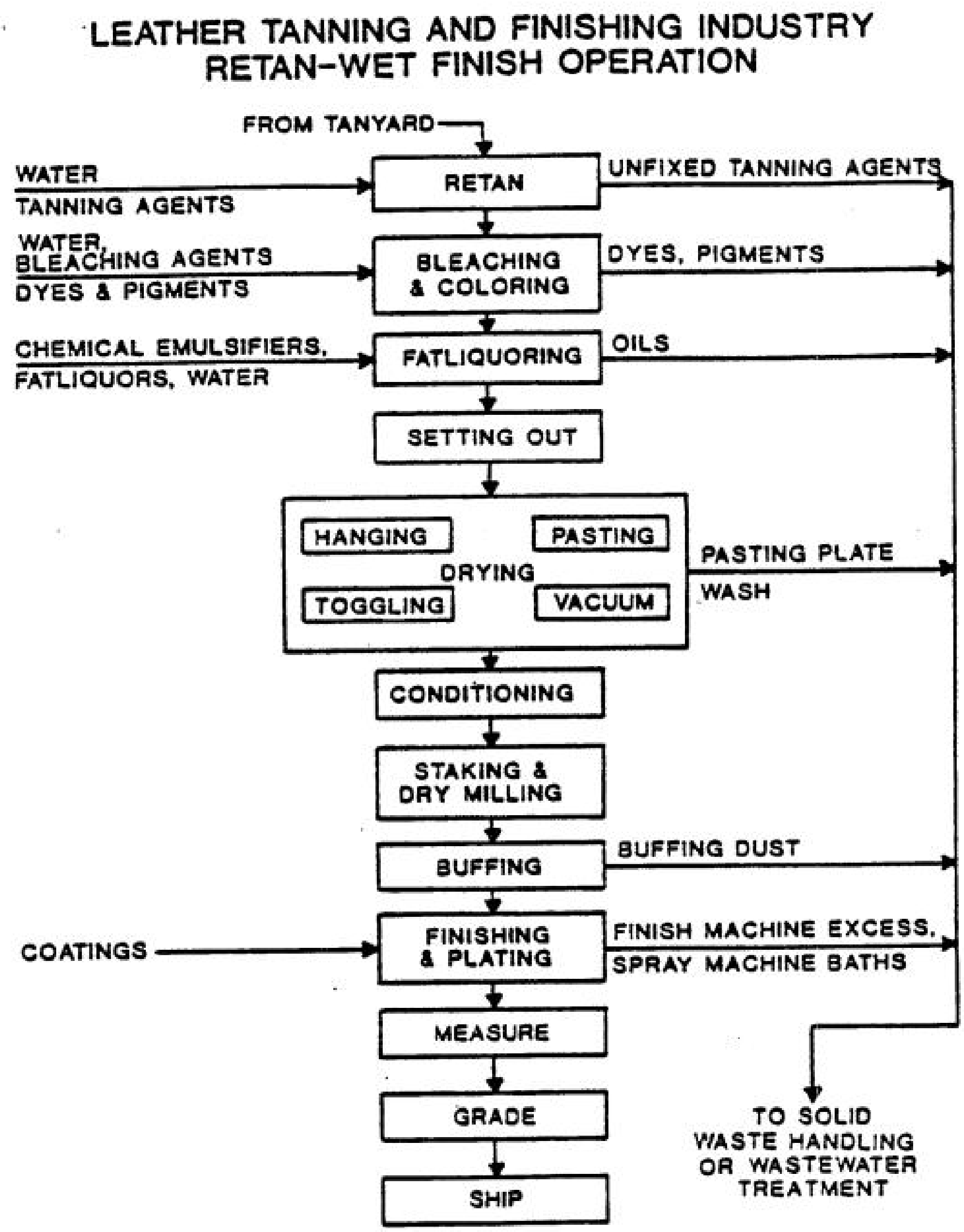

Figure 3. Retan Wet Finish Operation (Source: USEPA)

Retanning is used to give the leather certain special characteristics (different degrees of flexibility) which are lacking after the initial tanning step. The most common retanning agents are chromium, vegetable extracts (used to minimize variation between different parts of the chromium tanned hide), and syntans (used for softer side leathers and in making white or pastel leathers).

In the sole leather industry, sodium bicarbonate and sulfuric acid are used to bleach the leather after tanning.

Coloring involves combining dyes (usually aniline based) with the tanned skin fibers to form an insoluble compound. Dyes are added in the retanning wheels. Animal or vegetable fatliquors are added to replace the natural oils lost in the beamhouse and tanyard processes.

Finishing includes all operations performed on the hide after fatliquoring, and includes finishing to enhance color and resistance to stains and abrasions, smoothing and stretching the skin, drying, conditioning, staking, dry milling, buffing, and plating.

Figure 4 is a flow diagram showing all three tannery operations/processes.

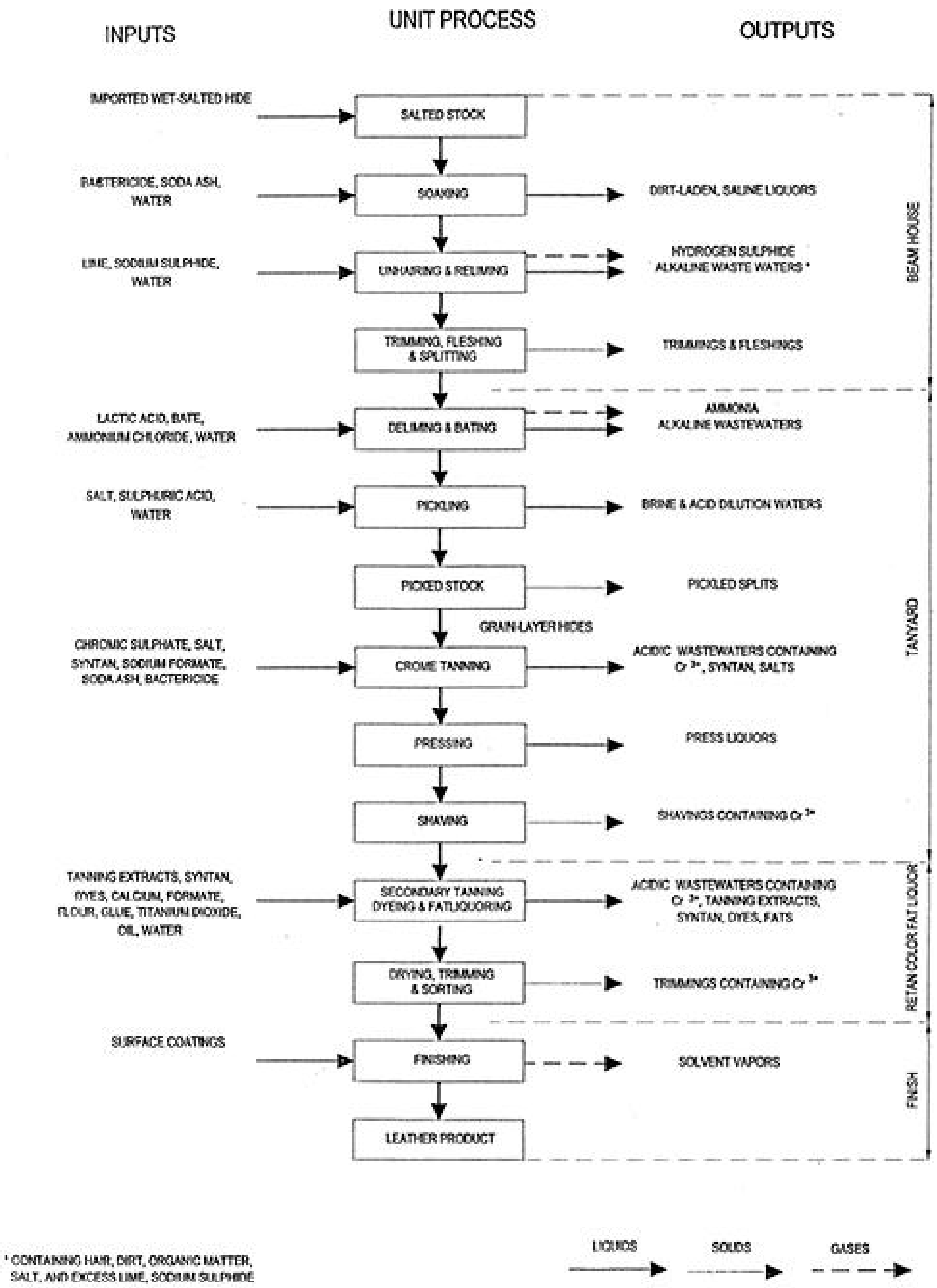

Figure 4. Schematic Diagram of All Major Tannery Operations and Processes (Source: USEPA)

1.5. Leather Tanning Industry Subcategories

Table 1 indicates that there are tannery nine subcategories which have been identified based on distinct combinations of raw materials and leather processing operations. Table 2 summarizes the raw materials and processes used by the subcategories, which are described in detail in the following sections.

LEATHER TANNING AND FINISHING INDUSTRY SUBCATEGORIES

Subcategory	Title
1	Hair Pulp, Chrome Tan, Retan-Wet Finish
2	Hair Save, Chrome Tan, Retan-Wet Finish
3	Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish
4	Retan-Wet Finish (Sides)
5	No Beamhouse
6	Through-The-Blue
7	Shearling
8	Pigskin
9	Retan-Wet Finish (Splits)

Table 1. Leather Tanning and Finishing Industry Subcategories (Source: USEPA)

SUBCATEGORY RAW MATERIALS AND PROCESSES

		Major Tanning and Finishing Steps		
Subcategory	Raw Materials	Beamhouse	Tanyard	Retan-Wet Finish
1	Cattlehide Deer, Elk, Moose	Hair Pulp	Chrome Tan	Yes
2	Cattlehide Calfskin	Hair Save	Chrome Tan	Yes
3	Cattlehide Calfskin	Hair Save or Pulp	Non-Chrome Tan	Yes
4	Blue Sides (cattlehide, pigskins)	--	--	Yes
5	Unhaired and Pickled Cattlehides, Sheepskins, Goatskins	--	Chrome or Non-Chrome Tan	Yes
6	Cattlehide	Hair Pulp	Chrome Tan	No
7	Shearlings (wool-on)	--	Chrome or Non-Chrome Tan	Yes
8	Pigskins	Hair Pulp	Chrome or Non-Chrome Tan	Yes
9	Blue Splits (drops) (cattlehide)	--	--	Yes

Table 2. Tannery Subcategory Raw Materials and Processes

1.5.1. Subcategory 1 -- Hair Pulp/Chrome Tan/Retan-Wet Finish

These are the tannery facilities which primarily process raw or cured cattle or cattle-like hides into finished leather by chemically dissolving the hair (hair pulp), tanning with trivalent chromium, and retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers, garments, upholstery, gloves, and lining material.

1.5.2. Subcategory 2 -- Hair Save/Chrome Tan/Retan-Wet Finish

These are the tannery facilities which primarily process raw or cured cattle or cattle-like hides into finished leather by chemically loosening and mechanically removing the hair (hair save), tanning with trivalent chromium, and retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers, handbags, garments, and gloves.

1.5.3. Subcategory 3 -- Hair Save or Pulp/Non-Chrome Retan/Retan-Wet Finish

These are the tannery facilities which process raw or cured cattle or cattle-like hides into finished leather by chemically dissolving (hair pulp), or loosening and mechanically removing the hair (hair save); tanning primarily with vegetable tannins, although other chemicals such as alum, syntans, or oils may be used; and retanning and wet finishing. Primary uses for the final products of this subcategory include sole leather, laces, harnesses, saddle leather, mechanical strap and skirting leather, and sporting good leathers (basketballs, footballs, softballs, baseballs, etc).

1.5.4. Subcategory 4 -- Retan-Wet Finish (Sides)

These are the tannery facilities which process previously unhaired and tanned “wet blue" grain sides into finished'leather through retanning with trivalent chromium, syntans, vegetable tannins, or other tanning agents, coloring with dyes, and wet finishing processes including fatliquoring, drying (especially pasting frame or vacuum), and mechanical conditioning. Primary uses for the final products of this subcategory include shoe uppers, garments, and personal goods.

1.5.5. Subcategory 5 -- No Beamhouse

These are the tannery facilities which process previously unhaired and pickled cattlehides, sheepskins, or pigskins into finished leather by tanning with trivalent chromium or other agents, then retanning and wet finishing. Primary uses for the final products of this sub-category include garments, shoe uppers, gloves, and lining material.

1.5.6. Subcategory 6 -- Through-the-Blue These are the tannery

These are the tannery facilities which process raw or cured cattle or cattle-like hides only through the "wet-blue" tanned state by chemically dissolving or loosening the hair and tanning with trivalent chromium. No retanning or wet finishing is performed. The "wet blue" stock produced by this subcategory is subjected to further processing by plants in Subcategory 4 (grain sides) and plants in Subcategory 9 (splits).

1.5.7. Subcategory 7 -- Shearling

These are the tannery: facilities which process raw or cured sheep or sheep-like skins with hair intact into finished leather by tanning with trivalent chromium or other agents, retanning, and wet finishing. Primary uses for hair on sheepskins (shearling) include hospital products, wool lined suede coats and similar garments, or specialty footwear, and seat covers.

1.5.8. Subcategory 8 -- Pigskin

These are the tannery facilities which process raw or cured pigskins into finished leather by chemically dissolving the hair and tanning with tri valent chromium, then retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers and gloves.

1.5.9. Subcategory 9 -- Retan/Wet Finish (Splits)

These are the tannery facilities which process previously unhaired and tanned splits into finished leather through retanning and wet finishing processes that include coloring, fatliquoring, and mechanical conditioning. Primary uses for the final products of this subcategory include sueded leathers for garments, shoe uppers, and other specialty or personal goods.

1.6 Leather Tanning Industry Pollutants

It was introduced previously that the leather tanning industry generates the following pollutants: (a) conventional pollutants, such as, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), pH and oil and grease

(O&G); (b) non-conventional pollutants, such as ammonia, total Kjeldahl nitrogen (TKN), nitrate and sulfide; and (c) toxic pollutants, such as, 2,4,6 trichlorophenol, chloroform, 1,2 dichlorobenzene, 1,4 dichlorobenzene, ethylbenzene, methylene chloride (dichloromethane), naphthalene, pentachlorophenol, phenol, bis-(2-ethyihexyl) phthalate, toluene, heavy metals (chromium, copper, lead, nickel & zinc), and cyanide.

Beamhouse processes typically generate approximately 40 percent of the wastewater volume and approximately 60 percent of the pollutant load (except chromium) from a complete tannery. Washing and soaking produce large quantities of wastewater containing dirt, salt, manure, and other materials. Solvent degreasing, usually performed only on sheepskins and pigskins, generates animal fat and waste skin material, spent detergents, and solvents. Unhairing is performed in an alkaline medium. The hair from the hair save method is usually disposed of in a landfill; however, the hair pulp process completely dissolves the hair. This process is the most significant source of proteinaceous organic and inorganic (lime) pollutants characterized by a high pH (10-12), and substantial amounts of BOD, TSS, sulfides, alkalinity, and nitrogen.

Wastewater from tanyard operations contain.inorganic chemical salts, small amounts of proteinaceous hair and waste, and large amounts of ammonia from the bating process. Pickling generates a highly acidic waste (pH of 2.5-3.5) which contains salt. Spent chromium liquors contain high concentrations of tri-valent chromium in acid solution with low concentrations of BOD and TSS and elevated temperatures. Discharges, (blowdown) from vegetable tanning vats necessary to maintain vegetable tanning liquor quality is highly colored and contains significant amounts of BOD, COD, and dissolved solids.

The retanning and wet finishing processes generate wastes with additional quantities of trivalent chromium, tannins, sulfonated oils, and spent dyes, which are low in BOD and TSS, high in COD, and at elevated temperature.

The typical characteristics of the two major tannery wastes from India were analyzed and reported in below.

Parameter	Beam House Waste	Tan Yard Waste
pH	10.87	3.64
COD	10300 mg/L	7030 mg/L
BOD	1704 mg/L	526 mg/L
TSS	4076 mg/L	7592 mg/L
Sulfides	530 mg/L	0.629 mg/L
Total Chromium	180 mg/L	1100 mg/L
Ammonia	970 mg/L	200 mg/L
TKN	1238 mg/L	289 mg/L
Oil & Grease	284 mg/L	896 mg/L
Sulfates	4500 mg/L	6400 mg/L
Chlorides	3800 mg/L	6200 mg/L
Total Copper	0.06 mg/L	0.12 mg/L
Total Lead	<0.1 mg/L	0.2 mg/L
Total Nickel	0.6 mg/L	0.8 mg/L
Total Zinc	0.508 mg/L	0.434 mg/L
TDS	14670 mg/L	13890 mg/L

Appendix A documents the discharge limits of tannery effluents in France, Italy and India [35].

2. CONVENTIONAL TANNERY WASTE TREATMENT PROCESSES

The process schematic in Figure 5 illustrates the conventional technology basis for the pretreatment limitations. In addition to in-plant controls, the treatment technology consists of screening, catalytic oxidation of sulfides (as shown in the top portion of Figure 5) in segregated unhairing wastestreams (applicable to plants in Subcategories 1, 2, 3, 6, and 8, which incorporate sulfide unhairing operations), flow balancing equalization, pH correction, flocculation, and coagulation-sedimentation with lime for chromium control of the segregated tanyard and retan-wet finish wastewaters, and neutralization of the combined wastestream. Biological reactor such as extended aeration activated sludge, and secondary sedimentation are usually required for further removal of dissolved organic pollutants. Also required are the sludge treatment processes shown in the bottom left hand side of Figure 5. These treatment processes are described in the following sections.

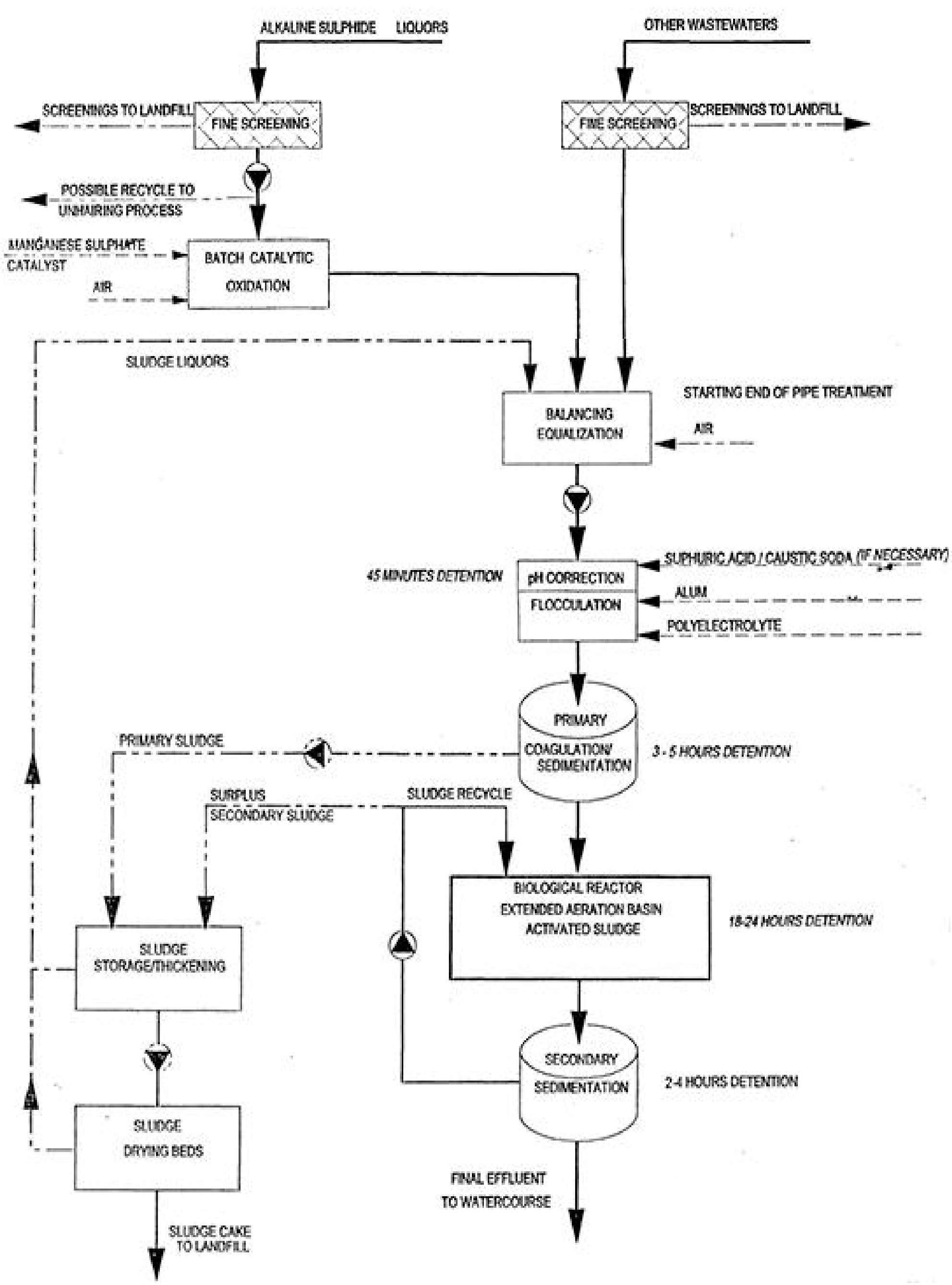

Figure 5. Conventional Best Practical Control Technology Achievable (BPCTA) for Tannery Waste Treatment

Many in-plant controls have often been found to be very cost effective in cleaning up industrial wastewater: In-plant controls applicable to the leather tanning and finishing industry include: (a) good housekeeping, (b) stream segregation, (c) water conservation, (d) recycle or reuse of concentrated liquors,, and (e) process modifications.

Manufacturing process modifications include alternative hide preservation methods, reduction of lime in unhairing operations, enzyme unhairing for hair-save operations, in-situ sulfide, oxidation, and ammonia substitution. Alternative hide preservation methods are designed to reduce the salt content of hides, and, in turn, wastewaters. These methods are intended to preserve the untanned hides for shorter periods of time. Alternative preservatives include refrigeration; boric acid; combinations of zinc, chlorite, or hypochlorite, and sodium pentachlorophenate; and sulfide combined with acetic acid. Of these, the latter two are the most economical. The reduction of lime reduces the amount of sludge produced and decreases the amount of acid required for pH neutralizaton. Enzyme unhairing, a method used for removal of hair when the hair will be sold, reduces the total nitrogen content in the unhairing wastes as compared with hair wastes that contain the fully dissolved hair from the hair-pulp method. In-situ sulfide oxidation is performed in the unhairing vessel and converts sulfide to sulfate with manganese (II) ion as a catalyst. It is most often used as an end-of-pipe treatment process and will be described in a later section. Substitution of ammonium sulfate by epsom salts (magnesium sulfate heptahydrate) can be used in deliming to reduce ammonia concentrations. However, loss in the hide weight, non-uniform grain of pickled bellies, and build-up of magnesium salts are sometimes experienced. Much more research will be needed in this area.

2.1 Conventional Treatment Processes For Segregated Waste Streams

Treatment processes that apply to the segregated waste streams from the beamhouse and from the tanyard and retan-wet finish operations are screening, sulfide oxidation, protein precipitation, and reduction and removal of ammonia, as described below.

2.1.1 Screening

Screening (Figure 5) is employed to protect downstream equipment and to remove suspended solids such as hair, buffing dust, and hide and leather scraps from fleshing and hide washing operations. Several types and sizes of screens are often installed, but should include bar screens (already in place at most tanneries) and fine screens (e.g., 0.040 inch openings) which few tanneries have in place. Operated correctly, screening equipment provides for efficient and necessary preliminary wastewater treatment. [23]

2.1.2 Sulfide Oxidation

Sulfide oxidation in tannery wastes is accomplished most often by catalytic oxidation (Figure 5), chemical oxidation, and precipitation. In catalytic oxidation of sulfide, the sulfide bearing wastes are collected in a suitable tank, manganese (II) ion is added, and the waste is aerated. Thiosulfate is the primary end product, although sulfite and sulfate also are present. Catalytic oxidation is widely used and has the advantage of reducing the alkalinity of unhairing liquor. Hydrogen, peroxide can also be used to oxidize sulfides in tannery wastes. When the pH is reduced to below 8.0, the addition of hydrogen peroxide causes sulfide to be oxidized to sulfur. The disadvantage of this method is the high cost of the chemicals. Sulfide precipitation by the addition of iron salts minimizes the possibility of oxidized sulfur reverting to sulfide. However, a large quantity of relatively expensive chemicals are required and more solid waste is generated. [24].

2.1.3. Ammonia Reduction

Ammonia reduction by physical means are most effective when applied to concentrated waste, such as the deliming waste stream. Evaporating water from the waste enables ammonium sulfate to be precipitated and removed. With the addition of phosphoric acid it is possible to precipitate the ammonia as insoluble calcium ammonium sulfate. Ammonium sulfate is also insoluble in a solution of ethanol and water. Additionally, reverse osmosis can be used to concentrate aqueous ammonium sulfate. [24, 25, 28].

The following figures (Figures 6-10) show the typical examples of conventional treatment processes for segregated waste streams:

Figure 6. Technology Schematic For In-Plant Control and Preliminary Treatment (Subcategories 1 and 2)

Figure 7. Technology Schematic For In-Plant Control and Preliminary Treatment (Subcategory 3)

Figure 8. Technology Schematic For In-Plant Control (Subcategory 4)

Figure 9. Technology Schematic For In-Plant Control and Preliminary Treatment (Subcategory 6)

Figure 10. Technology Schematic For In-Plant Control (Subcategories 5 and 7)

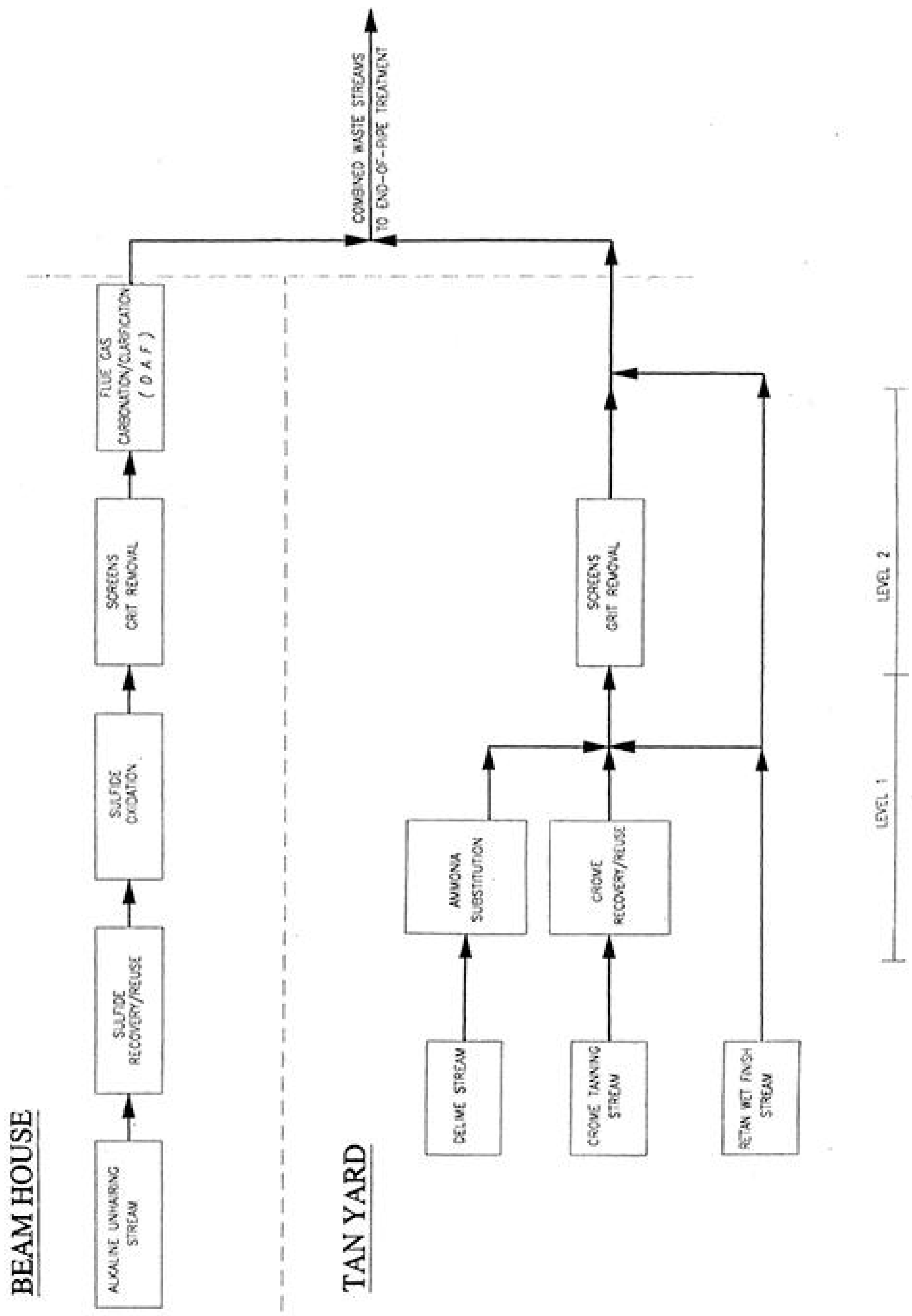

Figure 6. Technology Schematic For In-Plant Control and Preliminary Treatment (Subcategories 1 and 2)

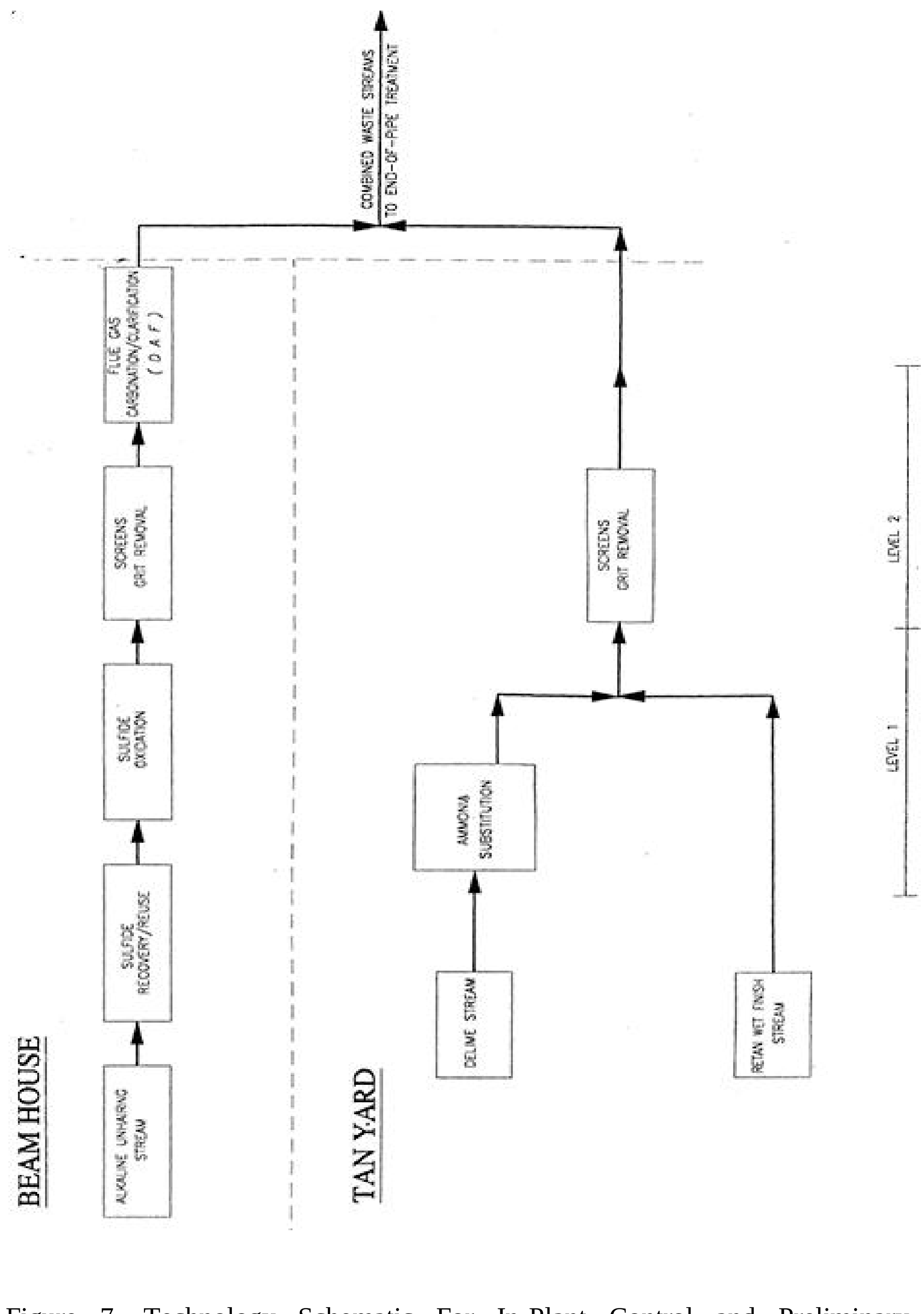

Figure 7. Technology Schematic For In-Plant Control and Preliminary Treatment (Subcategory 3)

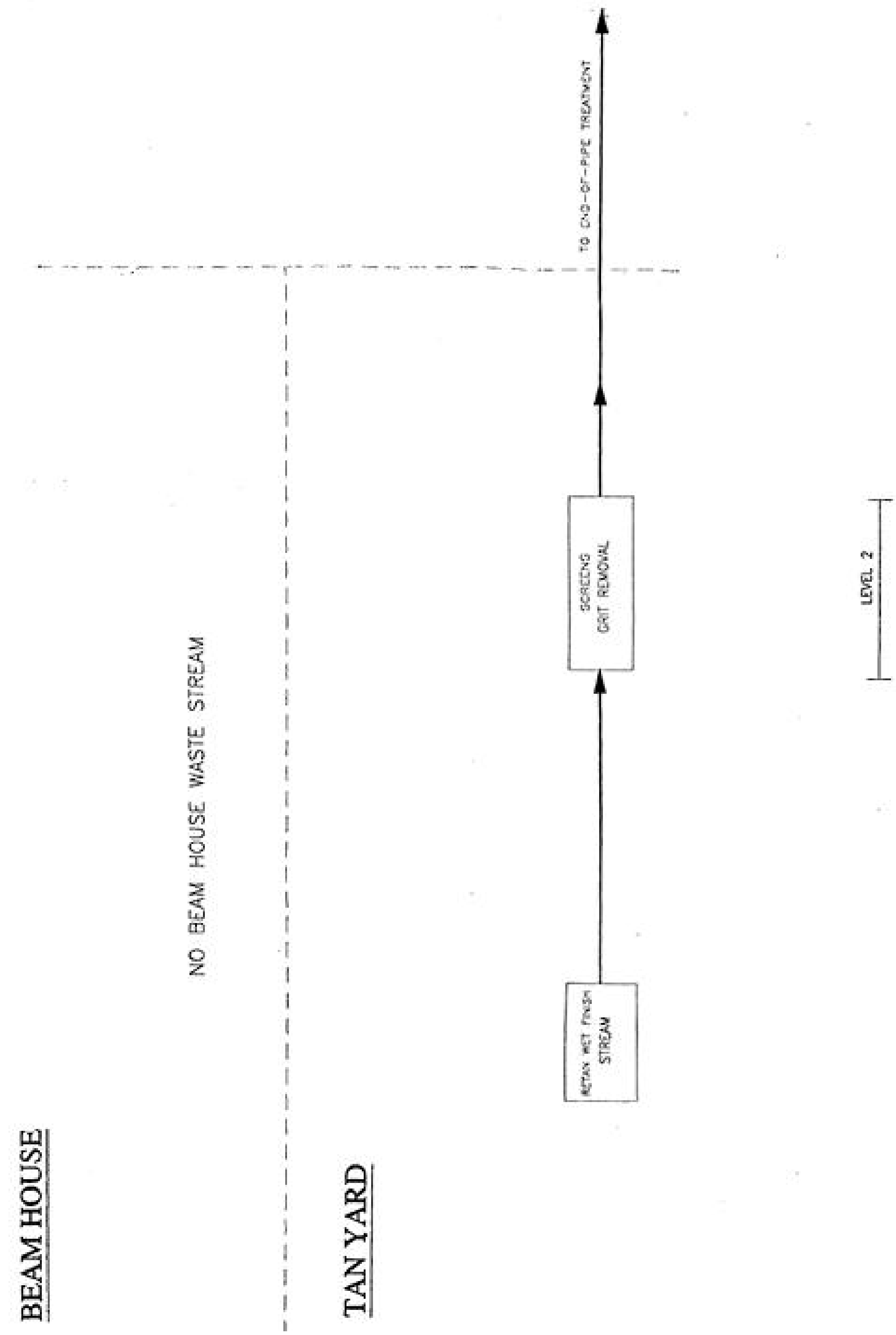

Figure 8. Technology Schematic For In-Plant Control (Subcategory 4)

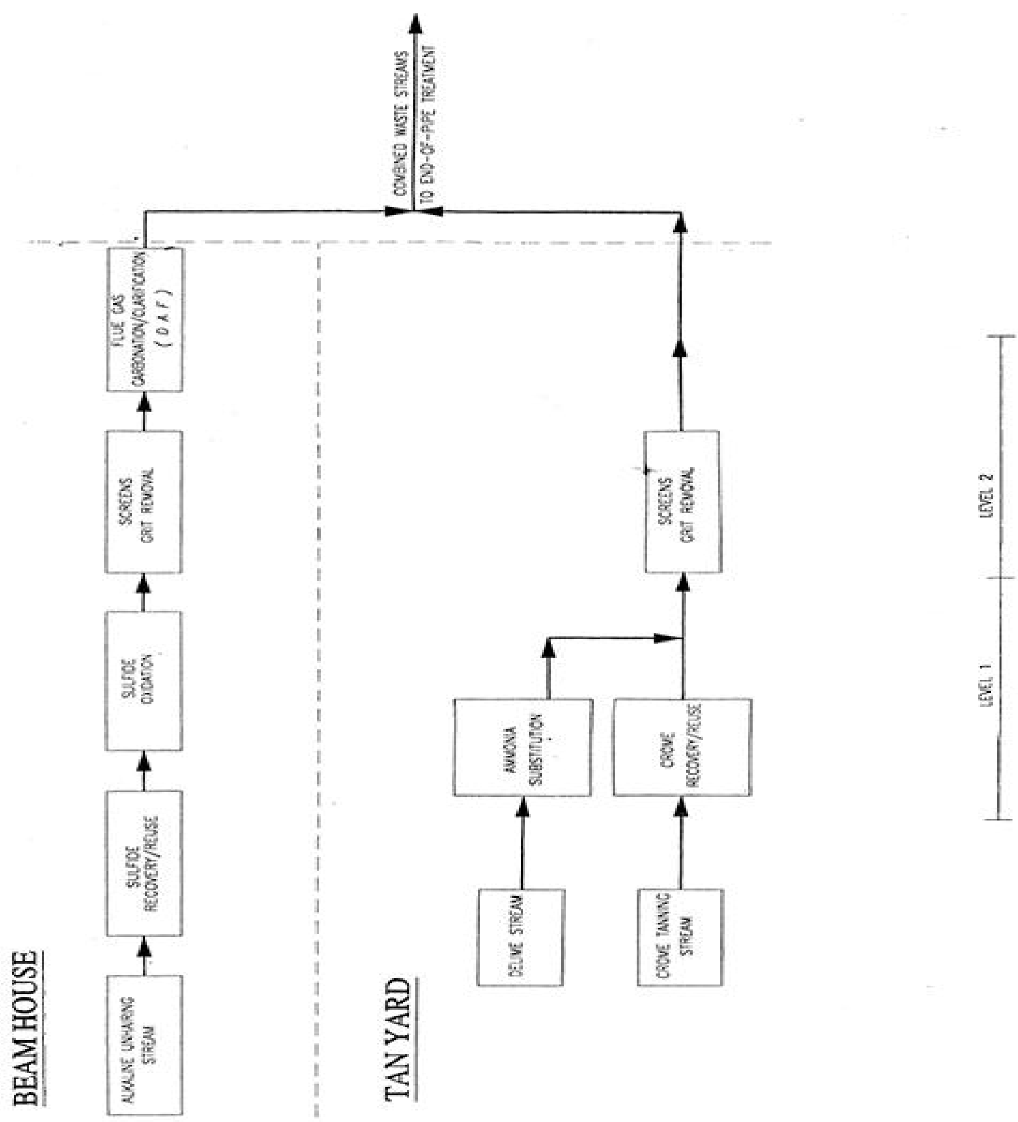

Figure 9. Technology Schematic For In-Plant Control and Preliminary Treatment (Subcategory 6)

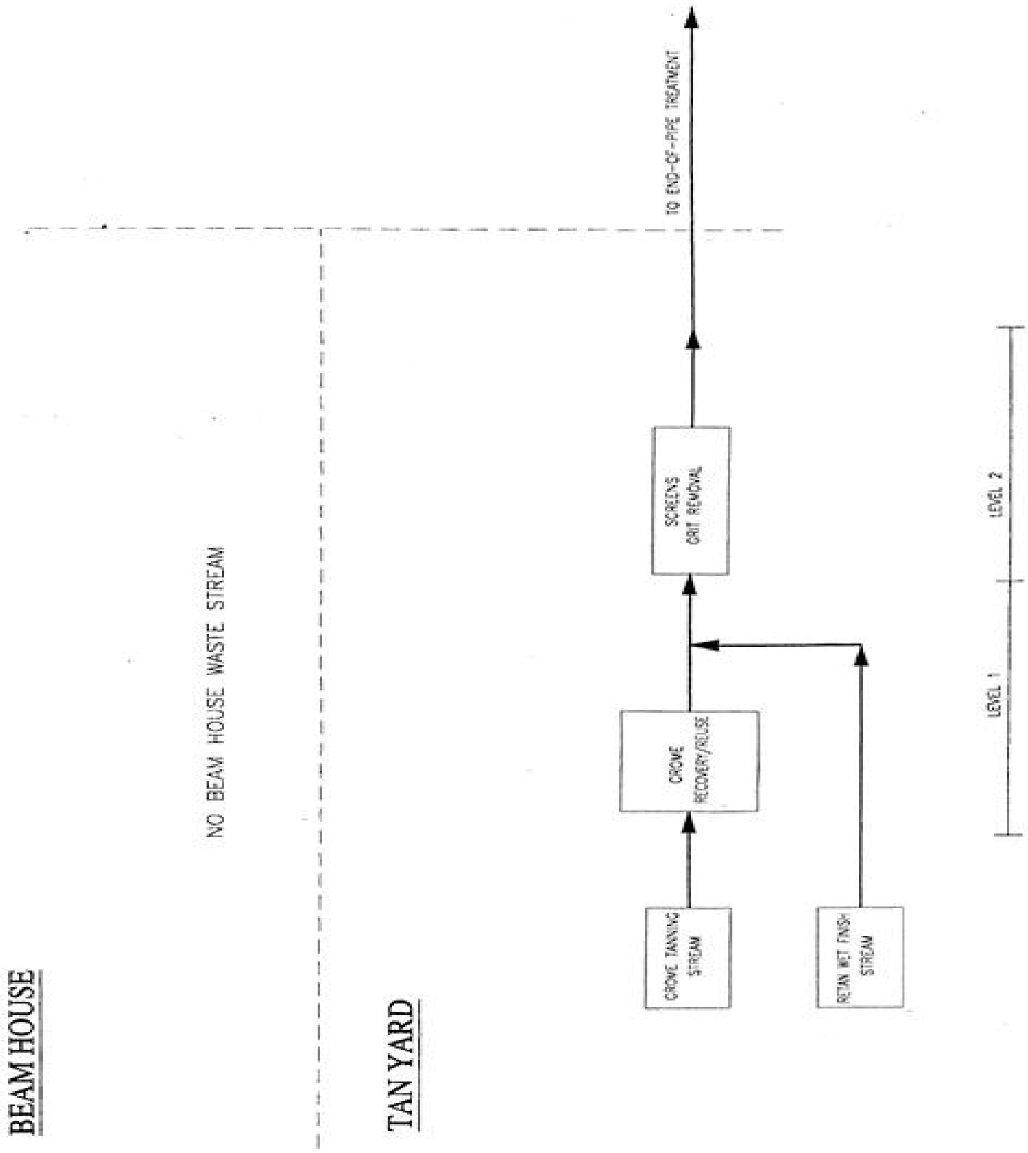

Figure 10. Technology Schematic For In-Plant Control (Subcategories 5 and 7)

2.2. End-Of-Pipe Wastewater Treatment Processes and Sludge Treatment Processes

The end-of-pipe treatment processes are applied to entire waste streams and may include flow equalization, sedimentation, coagulation-sedimentation, biological treatment, and filtration, as shown in Figure 11, and 12. [23-25].   Sludge treatment is also an important waste treatment step representing about 50% of total waste treatment costs. [2-27]. The top portion of Figure 11 illustrates the flow diagram of a conventional best available technology (BAT) which is introduced in the following Sections 2.2.1 through 2.2.6 , and discussed in Section 2.3.   Figure 12 is a simplified overall flow diagram showing (a) the in-plant control, (b) preliminary treatment, (c) the end-of-the-pipe wastewater treatment train, and (d) the sludge treatment of a general tannery waste treatment system based on the conventional best available technology economically achievable (BATEA, or simply BAT).

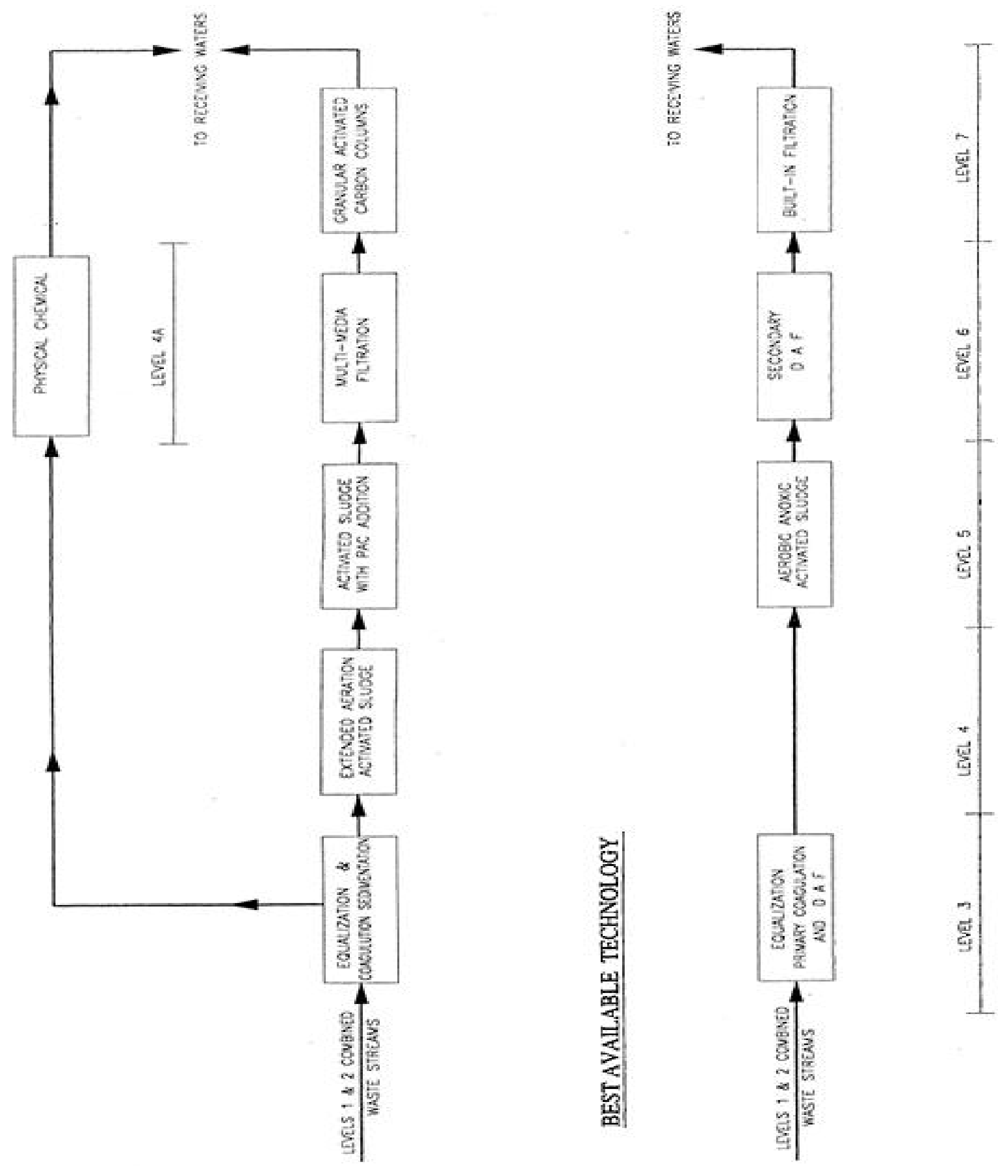

Figure 11. Technology schematic for end-of-pipe wastewater treatment of all subcategories based on best available technology economically achievable (BATEA, or BAT) and a comparison between conventional BATEA (top portion) and innovative BATEA (bottom portion)

2.2.1. Flow Equalization and Neutralization

Flow balancing and equalization process improves the consistency of other treatment processes performance by dampening flow surges, diluting slugs of concentrated wastes, partially neutralizing high and low pH waste fractions, and providing a relatively constant rate of flow to downstream treatment processes. [23]

2.2.2. Sedimentation

Sedimentation is one of the most widely used processes to treat individual and combined wastewater streams. Primary clarification removes suspended solids from tannery wastewater that are sources of BOD, COD, TKN, and certain toxic pollutants, particularly chromium. [23]

2.2.3. Chemical Coagulation-Sedimentation

Chemical coagulation process with alum, lime, and polymer significantly improves the performance of sedimentation in removing suspended solids, chromium, and other pollutants in the waste stream. When applied to segregated waste streams, coagulation-sedimentation provides cost-effective pretreatment to achieve Pretreatment Standards of Existing Sources (PSES) and Pretreatment Standards of New Sources (PSNS). In conjunction with other treatment processes, this method has shown to be very effective in removing pollutants. [23]

2.2.4. Biological Treatment

Conventional biological treatment process removes colloidal and dissolved biodegradable organic matter, suspended solids, and some toxic pollutants. Trickling filters, lagoons, activated sludge, and rotating biological contactors (RBCs) are all biological treatment processes that may be employed. The activated sludge process generally is preferred due to its greater consistency in pollutant removal capability, especially its ability to operate more efficiently in cold weather. [11, 13-14]. Upgraded biological treatment incorporates nitrification capabilities and the addition of powdered activated carbon (PAC) to aeration basins. [23]. Biological treatment by extended aeration activated sludge process with very long detention time (Figure 5) may further convert ammonia to nitrate by bio-oxidation.

2.2.5. Filtration in deep bed granular media filters is a physical-chemical process that involves removal of residual suspended solids by different filtered media, such as different grades of sand and anthracite coal. Because of the relationship between suspended solids levels and total chromium, multimedia filtration results in additional removal of chromium. The granular media can be sand, or multi-media, or even granular activated carbon (GAC). [23]

2.2.6. Solids Handling and Disposal

Sludge thickening is designed so that smaller and more efficient process equipment may be used in dewatering the sludge. Water removal and the corresponding reduction in weight and volume of the sludge is the main objective of the dewatering process. Common processes for dewatering include vacuum filtration, sludge drying on beds, centrifugation, and pressure filtration. Conditioning is performed to improve dewatering rates, solids capture, and compactability. Stabilization of sludge reduces its putrescible and pathogenic characteristics, thereby reducing the impact to the environment upon disposal. [26-27].

2.3. Conventional Best Practical Control Technology Achievable (BPCTA) and Best Available Technology Economically Achievable (BATEA)

The waste treatment technologies presented in the above sections and shown in Figure 5 are of conventional Best Practical Control Technology Achievable (BPCTA) because the final end-of-the pipe process is secondary sedimentation, meaning it is a biological secondary treatment. BPCTA is affordable, practicable & technically feasible to an acceptable level. it is the government's judgment that the industry has no excuse not to adopt it.

If a tertiary filtration (including granular activated carbon filtration) step is added after secondary sedimentation clarification (shown in Figure 12), it becomes an advanced tertiary treatment system adopting the Best Available Technology Economically Achievable (BATEA). BATEA is much better than BPCTA, but more expensive than BPCTA. It is the government's judgment that the industry still can afford it although the industry may disagree. BATEA usually is highly recommended but not enforced by the government.

Different levels of tannery waste treatment from Level 1 to Level 7 are graphically illustrated in Figures 7 to 11, and the effectiveness of various levels of wastewater treatment is listed in Table 3 (Source: USEPA).

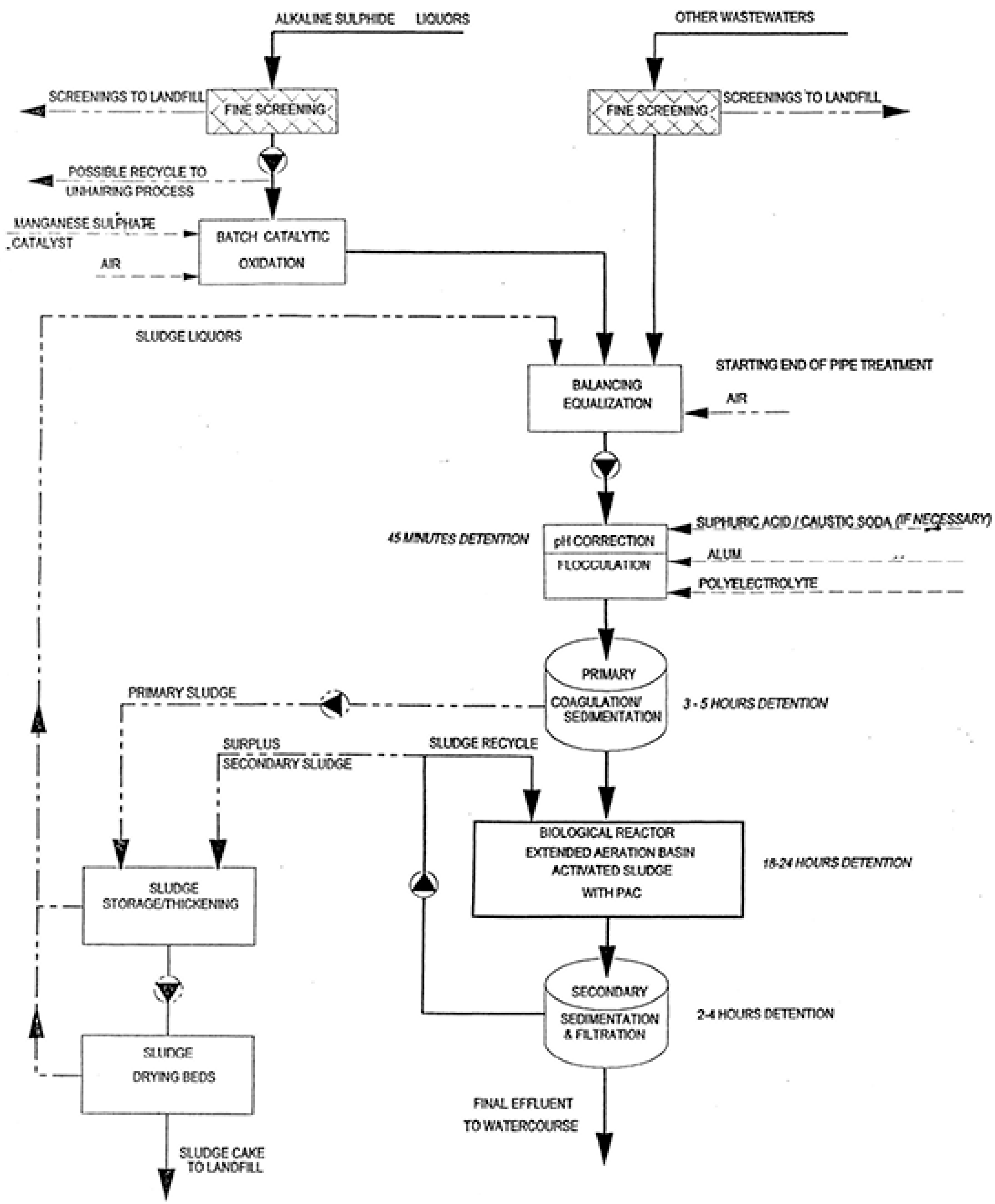

Figure 12. Conventional Best Available Technology Economically Achievable (BATEA) for Tannery Waste Treatment.

POLLUTANT PARAMETER	WASTE STREAM SEGREGATION (%) BEAMHOUSE	WASTE STREAM SEGREGATION (%) TANYARD	PERCENT REMOVALS FOR TREATMENT LEVELS 1 & 2 BEAMHOUSE	PERCENT REMOVALS FOR TREATMENT LEVELS 1 & 2 TANYARD	PERCENT REMOVALS FOR COMBINED WASTE STREAMS TREATMENT LEVEL 3	RESIDUAL CONCENTRATIONS AFTER TREATMENT LEVEL (mg/l) LEVEL 4	LEVEL 5	LEVEL 6	LEVEL 7
Flow	40	60	---	---	---	---	---	---	---
BOD_5	65	35	60	0.0	60	40	20	14	6
TSS	69	31	65	0.0	60	60	25	16	3
COD	56	44	60	0.0	65	250	195	180	165
Oil & Grease	49	51	70	0.0	70	14	10	6	2
Total Chromium	0.0	100	0.0	80	to 2 ppm	1	0.5	0.33	0.25
Sulfide	100	0.0	100	0.0	---	---	---	---	---
TKN	46	54	65	*	0.0	40	20	15	14
Ammonia	0.0	100	0.0	67	0.0	10	5	5	5
Phenol	0.0	100	0.0	0.0	0.0	0.25	0.1	0.1	0.1

Table 3. Effectiveness of Tannery Wastewater Treatment at Various Treatment Levels (Source: USEPA)

The problems of current environmental technologies (BPCTA & BATEA) for tannery waste treatment are : (a) primary coagulation-sedimentation clarification (with 3 to 5 hours of detention time which is too long); (b) upgraded biological extended aeration activated sludge process (with 18 to 24 hours of detention time which is too long) with or without addition of powdered activated carbon (PAC); (c) secondary sedimentation clarification (with 2 to 4 hours of detention time which is too long) plus multi-media filtration or GAC; (d) land space requirement is extremely high due to overall long detention time (21 to 29 hours) and large foot-print for waste treatment; (e) capital cost is very high due to long overall detention time (21 to 29 hours) for waste treatment, so they are not really economically feasible; (e) non-conventional pollutants (nitrate, sulfide) and toxic pollutants (volatile toxic organics, chrome, etc.) cannot be efficiently and economically removed; and (f) air pollution may still be caused by hydrogen sulfide and land pollution may still be caused by heavy metals, such as chromium, in the waste sludge, due to complexity of the overall treatment train.

3. LENOX INSTITUTE OF WATER TECHNOLOGY (LIWT) INNOVATIONS APPLIED TO SUSTAINABLE INDUSTRIAL WASTE TREATMENT USING LEATHER TANNING INDUSTRY AS AN EXAMPLE

3.1 Dissolved Air Flotation (DAF) and Combined Dissolved Air Flotation and Filtration (DAFF)

The largest contribution of the Lenox Institute of Water Technology (LIWT) is development of a series of high-rate, circular dissolved gas flotation (DGF) process equipment for worldwide applications in water, wastewater and sludge treatment. All circular DGF process equipment developed by the LIWT have been marketed and installed by Krofta Engineering Corporation (KEC) and its associated companies around the world. Dr. Milos Krofta was the President of both LIWT and KEC. The senior author, Dr. Lawrence K. Wang, was appointed by the US government to serve the United Nations Industrial Development Organization (UNIDO) as a Senior Advisor with a mission of transferring American environmental technologies (including the high-rate circular DGF) to developing countries for their sustainable industrial development.

Dissolved gas flotation (DGF) is a process involving pressurization of gas at 25 to 95 psig for dissolving gas into water, and subsequent release of pressure (to one atm) under laminar flow hydraulic conditions for generating extremely fine gas bubbles (20-80 microns) which become attached to the impurities to be removed and rise to the water surface together. The impurities or pollutants to be removed are on the water surface are called float or scum which scooped off by sludge collection means. The clarified water is discharged from the flotation clarifier's bottom. The gas flow rate is about one percent of influent liquid flow rate. The attachment of gas bubbles to the impurities can be a result of physical entrapment, electrochemical attraction, surface adsorption, and/or gas stripping. The specific gravity of the bubble-impurity agglomerate is less than one, resulting in buoyancy or flotation (i.e. Save-All).

If air, ozone, nitrogen, pure oxygen, carbon dioxide, air-ozone mixture, etc. are used for DGF operation, then the DGF becomes dissolved air flotation (DAF), dissolved ozone flotation (DOF), dissolved nitrogen flotation (DNF), dissolved oxygen flotation (DOF), dissolved carbon dioxide flotation (DCDF), dissolved air-ozone flotation (DAOF), respectively. It is noted, however, that flotation process can also be applied to oil-water separation [24], plastic-water separation, plastic-air separation, fiber-water separation [28], etc. without the use of dissolved gas bubbles at all.

All high-rate circular DGF process equipment have been designed based on the patented "zero-velocity design concept" which is explained elsewhere [29].

Figures 13 and 14 illustrate a simple flow diagram and a bird's view of the world's most popular circular DAF (or DGF) process equipment, commercially known as Krofta Supracell. Today there are over 2000 Supracell DAF installations around the world. The theory, principles, detailed flow diagrams, design criteria, operational procedures, O&M, costs, etc. of Krofta Supracell DAF can be found from the authors' recent literature [7-11, 19-22], so these technical information and cost data will not be repeated here. Circular Supracell DAF can be used as primary flotation clarification, secondary flotation clarification, or flotation sludge thickening for replacing conventional primary sedimentation clarification, secondary sedimentation clarification, and gravity sludge thickening, respectively. The size, capital cost, and O&M costs of a process equipment is almost proportional to the process equipment's detention time (DT). The DT of a high-rate Supracell DAF is only 15 to 20 minutes in comparison with a conventional sedimentation clarifier requiring 2 to 4 hours of DT. The cost savings when using Supracell DAF is obvious. In addition, all Supracell DAF units are very shallow. When the design flow rates increase, the Supracell DAF only increases its diameter. The per unit area ("per square foot" or "per square meter") unit weight of Supracell DAF is only lighter than the unit weight of a small compact car, so it can be installed on a building's roof top, or in the mid-level of a plant facility. Accordingly the innovative DAF may have a "zero foot-print", if it is required. Figure 15 shows how two Supracell DAF clarifiers (Model SPC 55 and Model SPC 30) achieve their almost "zero foot-print" requirement due to its extremely shallow outdoor stainless steel construction. Supracell DAF Model 55 has a diameter of 55 ft (16800 mm), a depth of 27 in. (685 mm), and treats 7290 gpm (1662 m^3/hour) of wastewater flow; while Supracell DAF Model 30 has a diameter of 30 ft (9000 mm), a depth of 25.5 in. (650 mm) and treats 2090 gpm (477 m^3/hour) of wastewater flow. When two Supracell DAF clarifiers replace two conventional sedimentation clarifiers for both primary clarification and secondary clarification in Figure 5 (BPCTA tannery waste treatment system), the wastewater treatment efficient will remain the same, except that the capital cost, O&M cost, and facility foot-print will be lower, and the O&M will be easier due to its complete open tank stainless steel construction.

Another LIWT's proud innovation is development of a combined DAF-filtration (DAFF) package plant commercially known as Krofta Sandfloat, and graphically shown in Figure 16. The top portion of a Sandfloat DAFF unit is similar to a Supracell DAF, while the bottom portion is a circular automatic backwash filtration (ABF). The ABF can be a filter with sand, multi-media, or granular activated carbon (GAC). Since DAF is built on the top of filtration, a further reduction of foot-print can be realized. The largest full scale DAFF plant in operation is Pittsfield Water Treatment Plant with a design capacity of 37.5 million gallons per day (MGD) [8, 23]. Krofta Sandfloat DAFF is widely used as a tertiary wastewater treatment unit around the world due to its compact design, small foot-print, easy operation and maintenance (O&M) and low cost. Entire Sandfloat DAFF is automatically operated and monitored without operator's constant attention. Similarly when Supracell DAF clarifier replaces conventional primary sedimentation clarifier and Sandfloat DAFF replaces both secondary sedimentation clarification and filtration in Figure 12 (BATEA tannery waste treatment system), the wastewater treatment efficient will remain the same, except that the capital cost, O&M cost, and facility foot-print will be significantly lower, and the O&M will be easier due to its complete open tank stainless steel construction.

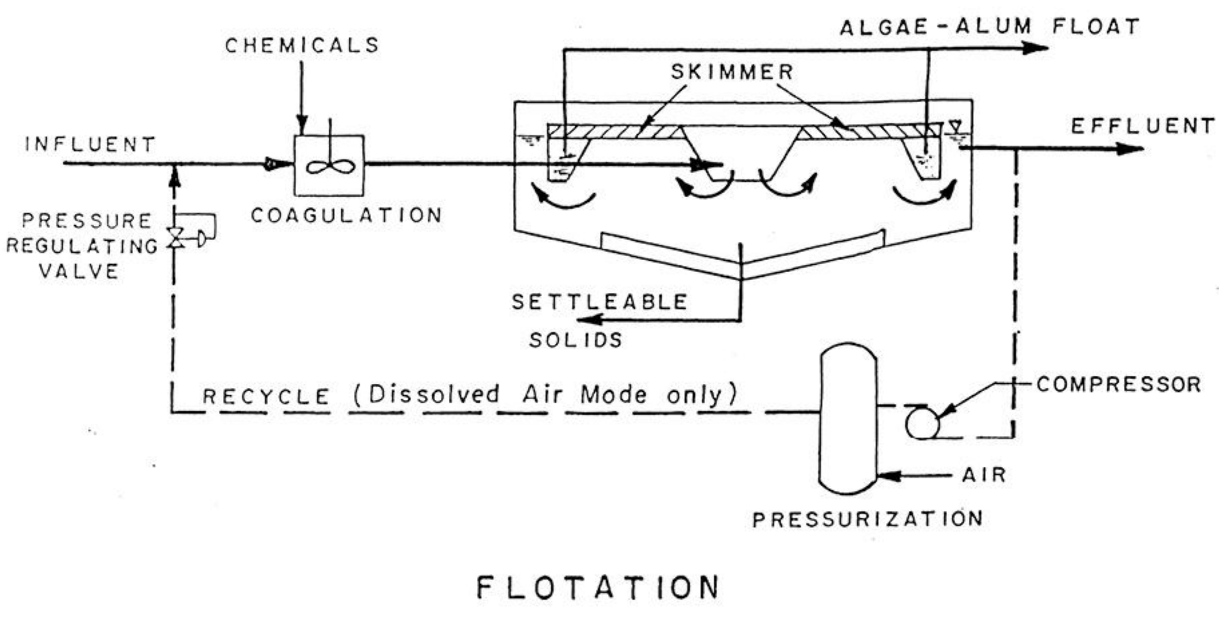

Figure 13. A Flow Diagram of a Shallow Circular High-Rate Krofta Supracell DAF Clarifier with Only 15 to 20 Minutes DT and Extremely Light Unit Weight.

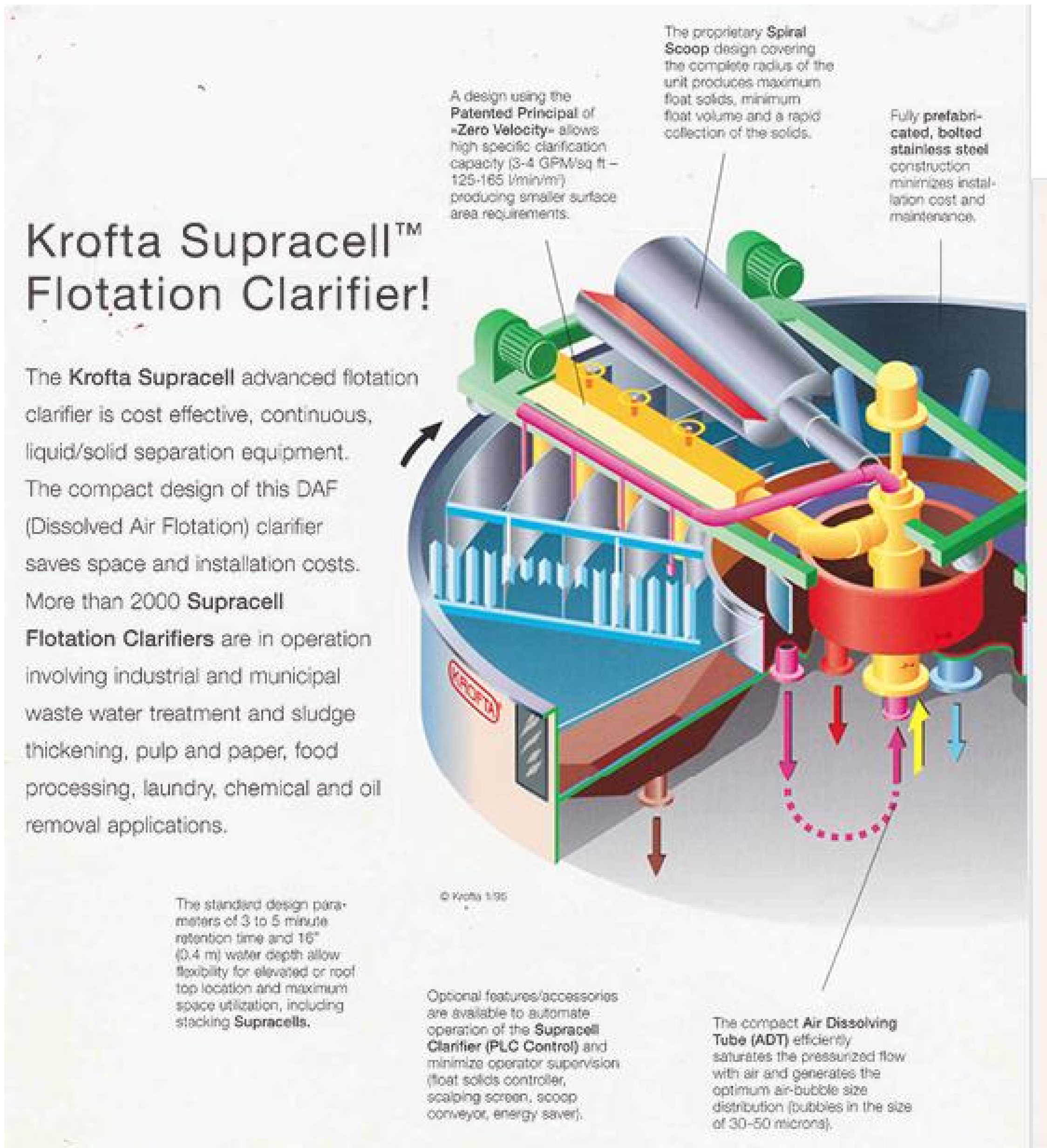

Figure 14. Bird's View of a High-Rate, Low Cost Krofta Supracell DAF Clarifier with Over 2000 Units in Operation Worldwide for Industrial and Municipal Wastewater Treatment and Sludge Thickening.

Figure 15. Almost "Zero Foot-Print" of Two Circular High-Rate Extremely Shallow Krofta Supracell DAF Clarifiers Installed in Spain

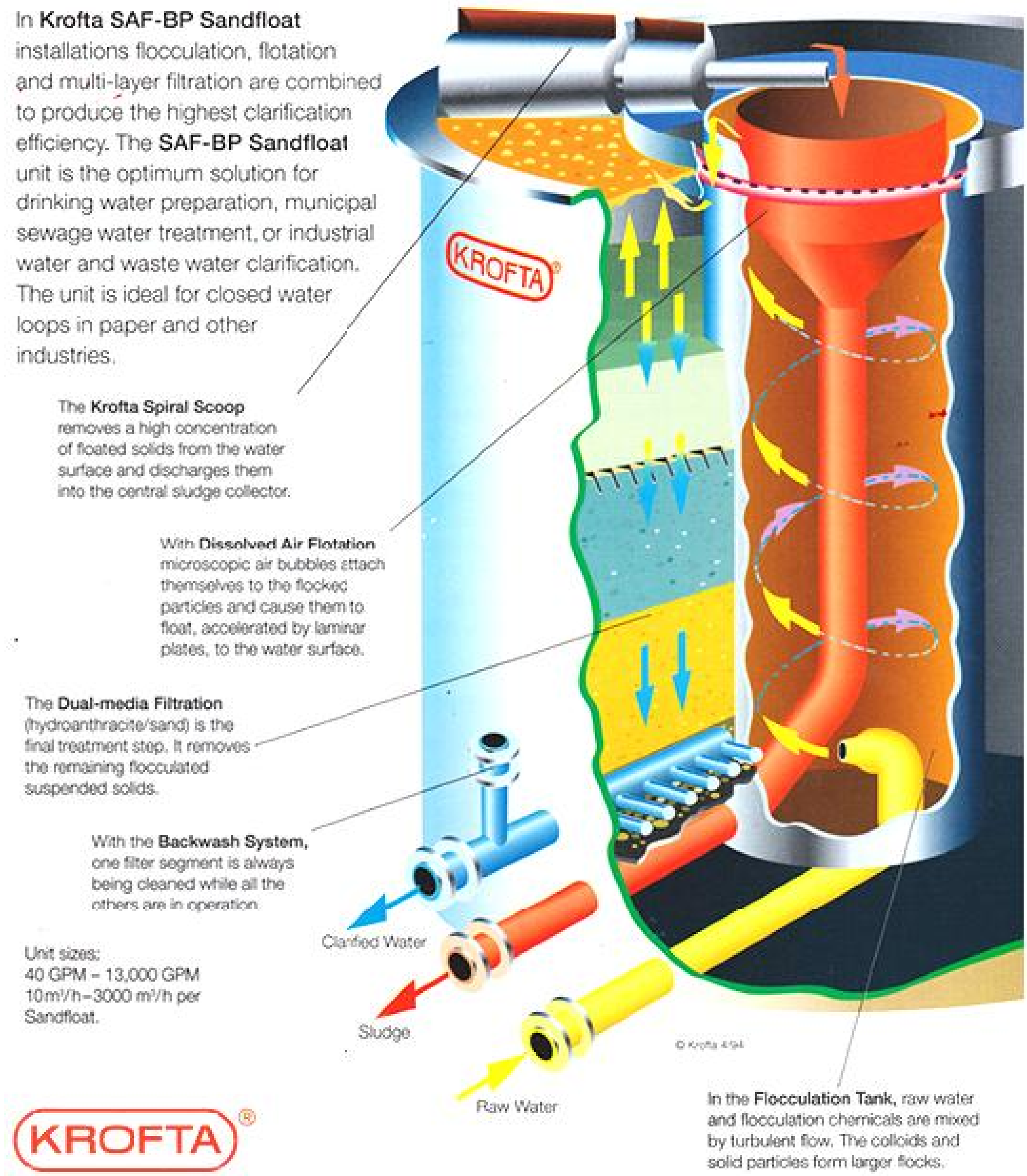

Figure 16. Krofta Sandfloat DAFF Clarifier with Both Dissolved Air Flotation and Automatic Backwash Filtration for Advanced Tertiary Wastewater Treatment

3.2 Combined DAF-DAFF Process System and Independent Physicochemical Wastewater Treatment System

Another sustainable environmental technology developed by the Lenox Institute of Water Technology (LIWT) is a circular combined Supracell DAF and Sandfloat DAFF system (or DAF-DAFF system with DAF on the top of DAFF), commercially known as KAMET (Krofta Advanced Municipal Effluent Treatment (KAMET), or KAMWT (Krofta Advanced Municipal Water Treatment (KAMWT), depending on its application. [8, 9, 10]. A full scale very compact KAMET/KAMWT unit (or DAF-DAFF unit each 20 ft. in diameter) which has been built to treat 1-MGD lagoon effluent for irrigation of a golf course is shown in Figure 17. Either conventional physicochemical waste treatment or conventional biological waste treatment with 1 MGD flow capacity will have a foot-print much much larger than 20-ft. diameter. The circular KAMET/KAMWT (DAF-DAFF) with extremely small foot-print will be a low cost solution to treating domestic, commercial or industrial wastewater.

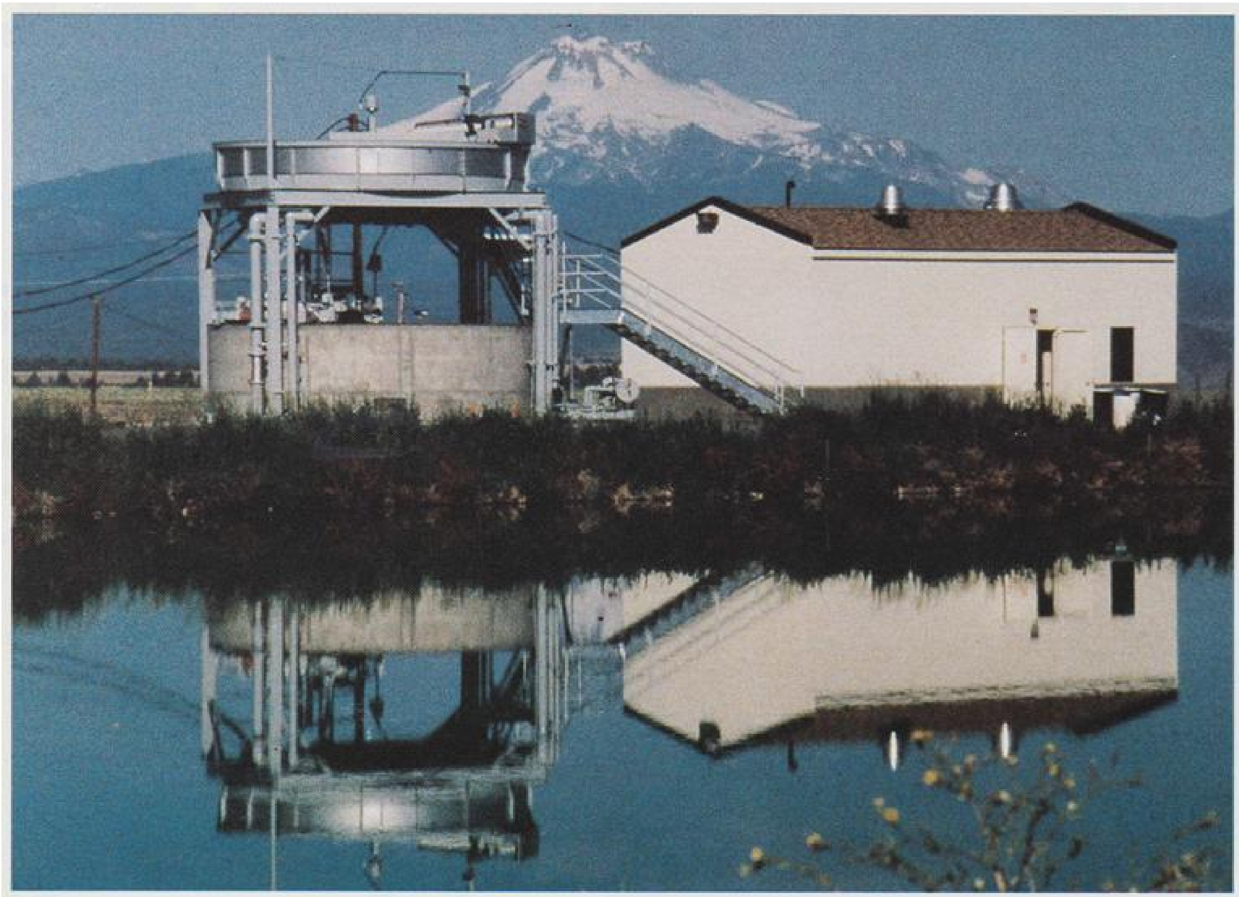

Figure 17. A Full Scale Krofta KAMET (DAF-DAFF, each with 20-ft diameter; design capacity = 1 MGD) Treating a Lagoon Effluent.

Normally the municipalities and industries adopt biological system or combined physicochemical-biological system for wastewater treatment due to the fact that biological processes are cheaper than physicochemical processes for the same wastewater flow and treatment efficiency. A complete physicochemical process system (also known as the "independent physicochemical wastewater treatment system (IPCWWTS)" is technically feasible to treat all wastewaters, however.

By definition, an Independent Physicochemical Wastewater Treatment System (IPCWWTS) is a wastewater treatment systems that utilizes physicochemical (PC) process technology other than biological process technology to obtain combined primary and secondary treatment efficiency for removals of mainly biochemical oxidation demand (BOD), chemical oxidation demand (COD), total suspended solids (TSS), and phosphate. Typically, an IPCWWTS uses combinations of preliminary treatment (flow equalization, bar screening, comminution, grit chamber, ammonia stripping), chemical precipitation/coagulation, primary clarification (primary sedimentation clarification or primary flotation clarification), secondary clarification (secondary sedimentation clarification, or secondary flotation clarification, without biological treatment), tertiary wastewater treatment (filtration, and/or granular activated carbon adsorption, ion exchange, PC oxidation, etc.), and disinfection. An innovative efficient primary flotation clarifier or a secondary flotation clarifier can be in any shape, circular or rectangular [9-13]. In general this IPCWWTS requires much less land area than conventional biological secondary treatment systems. Phosphors removal is inherent in this physicochemical process system.

Three Chinese taikonauts (i.e. astronauts) have just returned to the Earth this month (April 2022) after staying in their space station for six months. They used only physicochemical wastewater treatment and water recycle processes in the space.

Niagara Falls Wastewater Treatment Plant (NFWWTP), NY, USA, has been using conventional IPCWWTS since 1976, and has proven that IPCWWTS can adequately treat a combined municipal and industrial wastewater (average 48 MGD; peak 86 MGD flow) meeting all effluent discharge standards. Their physicochemical processing steps are briefly listed here for reference [15-17]:

1. Step 1. The wastewater for the City of Niagara Falls enters the plant in a large wet well from which four large pumps lift the water up and through screens that remove large solids. These solids go to a dumpster for disposal.
2. Step 2. The water then goes through a process in which all the grit is removed. Grit is comprised of solids that can pass through the screen and are dense enough to be readily removed through rapid settling. The grit is separated from the wastewater and sent to a dumpster for disposal.
3. Step 3. The wastewater flows into four sedimentation basins where chemicals are added to flocculate (an accumulation of particles) the lighter solids (called sludge) and allow them to settle out in the basins. The sludge is then pumped to one of two thickener basins, which allows it to settle further and become thick before being pumped to belt filter presses.
4. Step 4. The belt presses remove much of the water from the sludge by applying mechanical pressure, resulting in a filter cake that is disposed of.
5. Step 5. The wastewater then leaves the sedimentation basins and flows to the intermediate wet well where it is pumped up to the 28 carbon beds.
6. Step 6. The activated carbon removes the contaminants from the wastewater as it passes through the beds.
7. Step 7. The purified wastewater then leaves the beds and goes through treatment with hydrogen peroxide and sodium hypochlorite for odor control and disinfection prior to leaving the plant through the outfall, which enters the Niagara. (Source:

https://nfwb.org/app/uploads/2014/01/diagram2.gif). Appendix B shows the flow diagram of the City of Niagara Falls Wastewater Treatment Facility, New York, USA.

Conventional IPCWWTS using chemical coagulation and sedimentation clarification with long DT is technically feasible for wastewater treatment, but not economically feasible. NFWWTP treats combined municipal and industrial wastewater containing toxic substances, so they must adopt IPCWWTS. Other municipal wastewater treatment plants (WWTP) treat only or mainly domestic sewage, naturally adopt cheaper biological processes, such as activated sludge, trickling filter, or RBC.

Now LIWT/KEC have jointly developed an innovative IPCWWTS (commercially known as Krofta KAMET system) using low DT, high rate, low cost, small foot-print (or even zero foot-print) DAF and DAFF technology. KAMET which is a physicochemical process system can now compete with biological process systems for wastewater treatment. Figure 18 shows a BPCTA tannery waste treatment system adopting KAMET DAF-DAFF system for primary coagulation-primary flotation clarification (using Supracell DAF) and secondary flotation clarification and GAC filtration (using Sandfloat DAFF). A color photo of a KAMET DAF-DAFF system is shown in Figure 17.

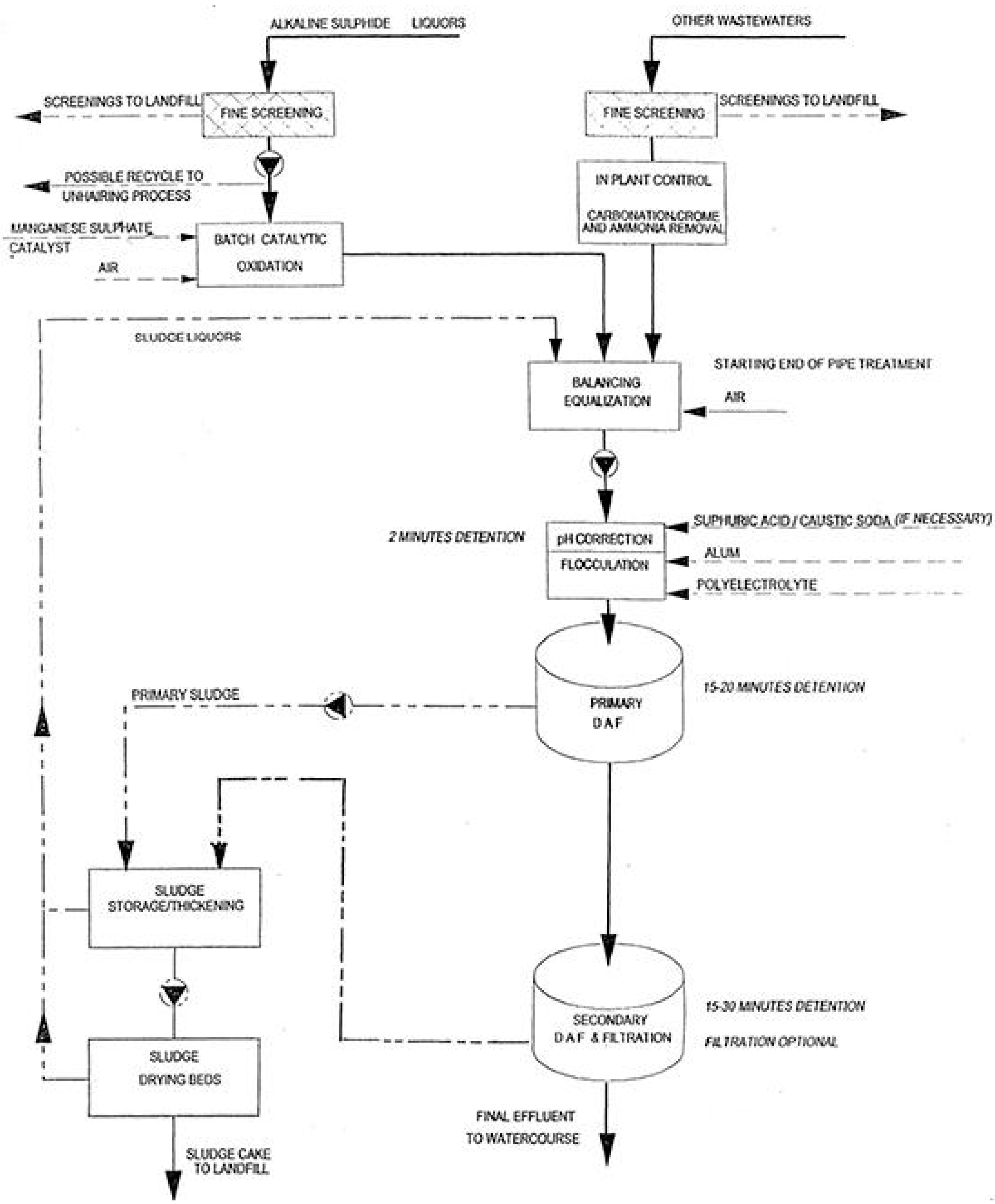

Figure 18. Adoption of Krofta KAMET (DAF-DAFF) System to be an Innovative Independent Physicochemical Wastewater Treatment System (IPCWWTS) for Tannery Waste Treatment Based on BPCTA.

3.3 Dissolved Protein Analysis, Dissolved Carbon Dioxide Flotation, Flue Gas Reuse, and Sustainable Industrial Development

Since dissolved protein in the leather tanning industry wastewater and food industry wastewater and can be efficiently removed by dissolved air flotation (DAF) and combined dissolved air flotation and filtration (DAFF) processes, an analytical method for analyzing dissolved protein in water and wastewater has been reported by the authors in "*Environmental Flotation Engineering*" [18]

The scientists and graduate students of Lenox Institute of Water Technology (LIWT) have successfully demonstrated that carbon dioxide from the tannery's boiler stack gas can be used as an inexpensive source of acid to neutralize caustic alkalinity and reduce pH. At the lower pH, dissolved protein in the beamhouse wastes flocculate with carbon dioxide forming chemical flocs. LIWT scientists further demonstrated that the chemical flocs can be easily harvested by conventional sedimentation clarification, vacuum filtration, or innovative dissolved carbon dioxide flotation (DCDF), or combined DAF-DCDF. [4-5].

The beamhouse waste contains high concentration of lime, proteins, sulfides, chlorides and sulfates. It is assumed that the dissolved proteins present in the beamhouse waste attach to the charged sites of the calcium carbonate flocs due to addition of flue gas containing carbon dioxide. The real chemical reaction is waiting for researchers to explore. Regardless of the real chemical reaction for precipitation of protein by addition of carbon dioxide from flue gas, the carbonation process reduces carbon dioxide release to the air, in turn, reduces the global warming problem. Sludge generated by carbonation and concentrated by dissolved carbon dioxide flotation (DCDF), or combined DAF-DCDF, or vacuum filtration, is rich in lime and protein and may be used as a soil conditioner or protein supplement in animal feed. Removing colloidal proteins also enhances coagulation-sedimentation, or coagulation-flotation downstream. Figures 6, 7, 9, 18 and 19 identify the location of carbonation process for dissolved protein removal before the beginning of the "end of pipe treatment" (balancing and equalization). This is a typical example of sustainable industrial development promoted by the United Nations Industrial Development Organization. [30]

Detailed experimental results of dissolved protein removal by carbonation using flue gas were reported by Lenox Institute Research Fellow LNSP Nagghappan [4] in his Master of Engineering (ME) thesis. 25 L/min of flue gas (carbon dioxide) was used to treat 600 mL of beamhouse wastewater for 30 seconds, then the wastewater sample was filtered for analysis. This carbonation process generated a huge amount of TSS at the ratio of 750 mL solids to 250 mL water in an Imhoff Cone. The bulky TSS were easily removed by vacuum filtration. The influent beamhouse pollutant concentrations were: COD 10300 mg/L; pH 10.87; TSS 4076 mg/L; sulfides 530 mg/L; and TDS 14670 mg/L. The effluent quality after carbonation and filtration was: COD 8467 mg/L; pH 7.3; TSS 550 mg/L; sulfide 530 mg/L; and TDS 15250 mg/L. It can be seen that the beamhouse wastewater COD (mainly dissolved protein) was reduced from 10300 mg/L to 8467 mg/L, the sulfide concentration remained unchanged, while TDS concentration increased slightly.

Further experimental results are reported in Section 3.5.2 Demonstration of Two-Stage PC-SBR for Sulfide Removal from Beamhouse Wastewater in First Stage, and Chromiun Removal from Tanyard wastewater in Second Stage. When ferrous sulfate was added to the carbonated waste at a dosage of 2.5 gm/L, the sulfides present in the wastewater was reduced from a value of 530 mg/L to 0.37 mg/L and additionally the COD of the beamhouse wastewater was further reduced by a value of 2300 mg/L. Thus the net COD reduction of the beamhouse wastewater, achieved by the pretreatment processes of combined carbonation and sulfide precipitation (by the first stage PC-SBR) was about 4300 mg/L. In other words, the COD value of the beamhouse wastewater was reduced from an influent value 10300 mg/L to 6000 mg/L. The readers are referred to Section 3.5.2 for more technical information.

3.4 Innovative Primary Flotation Clarification, Biological Aerobic-Anoxic Contact Stabilization and Secondary Flotation Clarification (DAF Or DAFF) Wastewater Treatment System.

Figure 18 illustrates that an IPSWWTS involving the use of primary flotation clarification (DAF) and combined secondary flotation clarification and filtration (DAFF) may be an environmental solution to developing countries which are satisfied with the best practical control technology achievable (BPCTA). [9-10] Figure 19, however, illustrates a better two-stage physicochemical and biological treatment system developed by the Lenox Institute of Water Technology (LIWT) [9, 11, 23]. The logic is simple and straight forward. Whenever economically affordable, the industrial nations should adopt the best available technology economically achievable (BATEA) instead of BPCTA. The choice of biological process selection is decided by the tannery manager. LIWT recommends the selection of the "innovative primary flotation clarification, biological aerobic-anoxic contact stabilization and secondary flotation clarification (DAF or DAFF) wastewater treatment system" shown in Figure 11 (bottom portion) and Figure 19. [4, 23]

The secondary DAF shown in Figure 11 and Figure 19 can also be DAFF instead. The filtration can be sand filtration, multi-media filtration, or GAC filtration. The readers are referred to latest literature [11, 31] for the recent advances in biological aerobic-anoxic contact stabilization process, and all flotation biological processes.

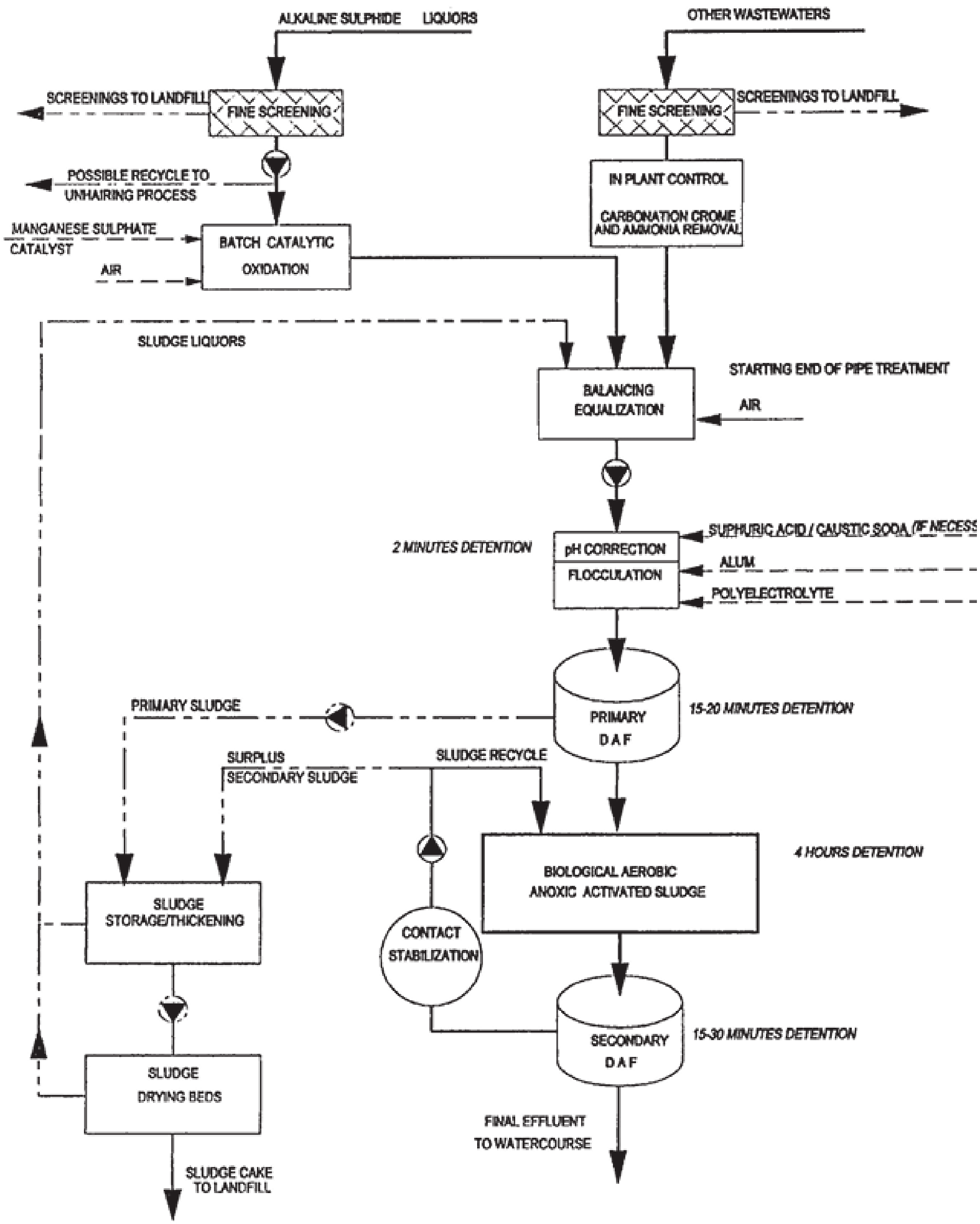

Figure 19. Adoption of Innovative Primary Flotation Clarification, Biological Aerobic-Anoxic Contact Stabilization and Secondary Flotation Clarification (DAF Or DAFF) Wastewater Treatment System To be BATEA [4, 23] (Secondary DAF can also be DAFF).

3.5 Removal of Sulfide Ions Using Ferrous Sulfate, Then Collection and Reuse of Ferrous Sulfide Sludge for Removal of Chromium (III) Ions from Wastewater

3.5.1 Innovative Physicochemical Sequencing Batch Reactor (PC-SBR)

This new innovation was patented by the authors in 1994 [32], and further investigated by the Lenox Institute of Water Technology (LIWT) [4,5, 33, 34]. The invented process, in part, was a physicochemical sequencing batch reactor (PC-SBR) using ferrous ions (ferrous sulfate, ferrous chloride, etc.) for precipitation and removal of toxic sulfide ions, and the freshly formed waste ferrous sulfide sludge is separated and reused for removal of positively charged toxic heavy metals (M^{+} or $M^{2+,}$ or M^{3+}) by reactions similar to ion exchange as follows:

ferrous ions Fe^{2+} + sulfide ions S^{2-}

= insoluble ferrous sulfide FeS (1)

insoluble ferrous sulfide FeS + (M^{+} or $M^{2+,}$ or M^{3+})

= metal sulfide + ferrous ions Fe^{2+} (2)

In the above PC-SBR reactions (1) and (2), both toxic sulfide ions S^{2-} and toxic metals (M^{+} or $M^{2+,}$ or M^{3+}) are removed as the insoluble metal sulfide [33]. The produced ferrous ions Fe^{2+} in reaction (2) may or may not be reused again in reaction (1).

3.5.2 Demonstration of Two-Stage PC-SBR for Sulfide Removal from Beamhouse Wastewater in First Stage, and Chromiun Removal from Tanyard wastewater in Second Stage

Conventional tannery waste treatment systems shown in Figures 2, 3, 6, 7, and 9, and innovative tannery waste treatment systems shown in Figures 18-19 adopt the application of catalytic oxidation process for oxidizing toxic sulfide ions using manganese sulfate as a catalyst.

LIWT professors and graduate students [3,4, 33, 34] have demonstrated that the authors' PSC-SBR [32] is technically and economically feasible for simultaneously removal of both toxic sulfide ions and toxic chromium ions in the tannery waste streams by a two stage PC-SBR process system shown by the above Reaction (1) and Reaction (2) , or the following Reaction (1a) and Reaction (2a), if ferrous sulfate is used in the first stage:

ferrous sulfate $FeSO_4$ + sulfide ions S^{2-}

= insoluble ferrous sulfide FeS + SO_4^{2-} (1a)

insoluble ferrous sulfide FeS + Cr^{3+}

= insoluble Cr_2S_3 + ferrous ions Fe^{2+} (2a)

ferrous ions Fe^{2+} + SO_4^{2-} = ferrous sulfate $FeSO_4$ (3)

The ferrous sulfate $FeSO_4$ formed in Reaction (3) can be reused if necessary.

After the first step of chemical precipitation, the next water-solid separation step of PC-SBR can be flotation, sedimentation, or filtration (including vacuum filtration or membrane filtration). In this tannery waste treatment, vacuum filtration was chosen for water-solid separation before the end-of-pipe treatment.

3.5.2.1 Sulfide Removal from Beamhouse Wastewater in First Stage

When the beamhouse waste containing 530 mg/L of toxic sulfide ions (from India) was subjected to sulfide removal by addition of ferrous sulfate in accordance with Reaction (1a), about 2.5 gram/L of ferrous sulfate was needed to reduce sulfide ions to less than 1 mg/L sulfide ion, meeting the effluent disposal standard for sulfides in India [3,4]. Even though the dosage of ferrous sulfate is high, the advantage of this two stage PC-SBR process is two folds: (a) reduction of sulfide can be achieved from the waste to a value much less than 2 mg/L (India effluent discharge standard), and thus the toxicity of sulfide is reduced; (b) the ferrous sulfide sludge formed by Reaction (1a) in the first stage can be recovered and be reused for the removal of toxic chromium ions in the tanyard waste from India according to Reaction (2a). Theoretically the amount of sulfide sludge produced in Reaction (1a) can be 100% reused for toxic chromium ions removal in Reaction (2a).

It was reported previously in Section 3.3 (Dissolved Protein Analysis, Dissolved Carbon Dioxide Flotation, Flue Gas Reuse, and Sustainable Industrial Development) that (a) The influent beamhouse pollutant concentrations were: COD 10300 mg/L; pH 10.87; TSS 4076 mg/L; sulfides 530 mg/L; and TDS 14670 mg/L; and (b) The effluent quality after carbonation and filtration was: COD 8467 mg/L; pH 7.3; TSS 550 mg/L; sulfide 530 mg/L; and TDS 15250 mg/L. It can be seen that the beamhouse wastewater COD (mainly dissolved protein) was reduced from 10300 mg/L to 8467 mg/L, the sulfide concentration remained unchanged, while TDS concentration increased slightly.

The carbonation and filtration effluent (with pollutant concentrations of COD 8467 mg/L; pH 7.3; TSS 550 mg/L; sulfide 530 mg/L; and TDS 15250 mg/L) was treated with 2515 mg/L of ferrous sulfate according to Reaction (1a). After reaction, large volume of black colored ferrous sulfide sludge was generated. Again vacuum filtration was an efficient water-solid separation method for harvesting the ferrous sulfide sludge, and producing a much better pre-treated first-stage PC-SBR effluent (COD 6020 mg/L; pH 6.82; TSS 530 mg/L; sulfide 0.317 mg/L; and TDS 14320 mg/L). It is noted that COD was further reduced from 8467 mg/L to 6020 mg/L, and sulfide was reduced from 530 mg/L to 0.317 mg/L, which was significant for the beamhouse wastewater treatment. [3, 4]

3.5.2.2 Chromiun Removal from Tanyard wastewater in Second Stage

A tanyard wastewater containing chromium, chlorides, sulfates and thick hairy substance from India was investigated by LIWT scientists [3,4]. The tanyard wastewater was very thick and contributed substantial amount of organic concentrations such as COD, TSS and BOD. Initially the hairy substances were removed by physical separation method (vacuum filtration), resulting in a great reduction of COD, BOD and TSS of the waste. The vacuum filtration effluent was then treated by the second stage PC-SBR (chemical ion exchange and vacuum filtration) using the harvested waste ferrous sulfide sludge (see Section 3.5.2.1) in accordance with Reaction (2a).

During the ferrous sulfide sludge harvested from the beamhouse waste treatment according to Reaction (1a) was added to the tanyard waste (all from India) for further treatment according to Reaction (2a), vacuum filtration was needed for water-solid separation at each step, and Reaction (2a) was valid only when ferrous sulfide sludge was still fresh.

The following are the tanyard waste pre-treatment results: (a) tanyard wastewater influent: COD 7030 mg/L; pH 3.64; TSS 7592 mg/L; chromium (III) 1100 mg/L; TDS 13890 mg/L; (b) tanyard wastewater influent after vacuum filtration: COD 4484 mg/L; pH 3.57; TSS 550 mg/L; chromium (III) 1100 mg/L; TDS 13555 mg/L; (c) tanyard waste treated by vacuum filtration, 1858 mg/L harvested ferrous sulfide sludge and 1 mg/L lime for pH adjustment according to Reaction (2a) and again vacuum filtration: COD 2610 mg/L; pH 6.52; TSS 520 mg/L; chromium (III) 0.2 mg/L; TDS 12400 mg/L.

It is noted above that the harvested ferrous sulfide sludge from beamhouse waste treatment according to Reaction (1a) was very useful to tanyard waste treatment for chromium and COD removals. At a ferrous sulfide dosage of 1857 mg/L, the chromium present in the waste was reduced from a value of 1100 mg/L to 0.2 mg/L and the COD of the tanyard waste was further reduced by a value of about 2000 mg/L. Thus a net COD reduction of the tanyard waste achieved by the PC-SBR pretreatment process (chemical ion exchange plus vacuum filtration) was about 5000 mg/L (from an influent COD value 7030 mg/L to an effluent COD value 2600 mg/L). Chromium reduction from 1100 mg/L to 0.2 mg/L was perfect.

Although the Lenox Institute of Water Technology (LIWT) experiments were conducted as physicochemical sequencing batch reactor (PC-SBR) mode, continuous process operation is also valid, and recommended.

It was estimated that the beamhouse Reaction (1a) pretreatment generated about 1457 mg/L of ferrous sulfide sludge, while the tanyard Reaction (2a) required 1857 mg/L of ferrous sulfide sludge to be reused for chromium removal. Additional 400 mg/L of ferrous sulfide sludge would be needed for completion of Reaction (2a) for reducing 1100 mg/L chromium to less than 2 mg/L (India effluent limit). This additional ferrous sulfide sludge was generated by mixing ferrous sulfate and sodium sulfide, which precipitated insoluble ferrous sulfide sludge within a period 3 minutes in the laboratory. In real full scale operation, the ferrous sulfate may be obtained from Reaction (3) for chemical cost saving. The researchers around the world are invited for further innovative research initiated and explored by LIWT.

3.6 Membrane Biological Flotation Reactor (MBFR)

The bottom portion of Figure 11 presents the best available technology economically achievable (BATEA) for treating tannery waste in all industrial countries. The final step of the end-of-pipe tannery waste treatment is filtration. The authors' recommended filtration is membrane filtration for further reduction of total dissolved solids (TDS).

The beamhouse effluent quality after carbonation and vacuum filtration was: COD 8467 mg/L; pH 7.3; TSS 550 mg/L; sulfide 530 mg/L; and TDS 15250 mg/L.

The beamhouse effluent quality after both carbonation-vacuum filtration and the first stage PC-SBR effluent was improved to: COD 6020 mg/L; pH 6.82; TSS 530 mg/L; sulfide 0.317 mg/L; and TDS 14320 mg/L.

The tanyard effluent quality after the second stage PC-SBR and vacuum filtration using the recycled ferrous sulfide sludge was improved to: COD 2610 mg/L; pH 6.52; TSS 520 mg/L; chromium (III) 0.2 mg/L; TDS 12400 mg/L.

It can be seen from the above experimental results that the remaining TDS concentration was still very high. Membrane filtration will be the only unit process for adequate reduction of TDS. [23-28]. However, membrane filtration alone, or membrane bioreactor (MBR) are too expensive to be feasible for tannery TDS removal. The BATEA developed by LIWT is a complete cost-effective membrane biological flotation reactor (MBFR) system using LIWT developed Supracell DAF, Sandfload DAF-DAFF and biological flotation aerobic-anoxic contact stabilization for pretreatment prior to membrane filtration. For further cost reduction, a MBFR package plant can be developed for use by the tanneries.

Since this publication is the authors' memoir, only the authors' research data regarding Lenox process equipment (Supracell DAF, Sandfloat DAFF, Krofta KAMET DAF-DAFF), Lenox process systems (IPSWWTS, PC-SBR, MBFR, biological flotation aerobic-anoxic contact stabilization, physicochemical-biological two stage flotation system, etc.) and other Lenox sustainable innovations (dissolved protein precipitation using carbon dioxide from flue gas, vacuum filtration of sludge, ferrous sulfate precipitation of sulfide ions, reuse of ferrous sulfide sludge for chromium ions removal, etc.) are introduced. Other manufacturers' process equipment, and process systems, such AquaDAF, Clari-DAF, vertical bioreactors, membrane bioreactors, etc. are equally feasible for tannery waste treatment. [1-7, 12-17, 28, 31, 35]

GLOSSARY OF TANNERY WASTE TREATMENT [1-6, 35-37]

AquaDAF: It is a rectangular dissolved air flotation (DAF) clarifier commercially available from SUEZ Water Technologies and Solutions, Richmond, VA 23229, USA.

Bar and fine screens: There are two types of bar screens (or racks). The most commonly used, and oldest technology, consists of hand-cleaned bar racks. These are generally used in smaller wastewater treatment plants (WWP). The second type of screen is the type that is mechanically cleaned, which is commonly used in larger facilities and the opening is flexible. If the opening is small, it is called fine screens.

Beamhouse operations: The operation consist of four typical sub-operations: (a) Side and trim; (b) soak and wash; (c) fleshing; and (d) unhairing. Side and trim is the cutting of the hide into two sides and trimming of areas which do not produce good leather. In soak and wash processes, the hides or sides are soaked in water for eight to twenty hours to restore the moisture that was lost during curing. Washing removes dirt, salt, blood, manure, and nonfibrous proteins. Fleshing is a mechanical operation which removes excess flesh, fat, and muscle from the interior of the hides. Cold water is used to keep the fat congealed. The removed matter is normally recovered and sold for conversion to glue. Unhairing involves using calcium hydroxide, sodium sulfhydrate, and sodium sulfide to destroy the hair (hair pulp) or remove hair roots (hair save), loosen the epidermis, and remove certain soluble skin proteins. A mechanical. unhairing machine is used to remove hair loosened by chemicals in the hair save process. Beamhouse operations typically generate approximately 40 percent of the wastewater volume and approximately 60 percent of the pollutant load (except chromium) from a complete tannery. Washing and soaking produce large quantities of wastewater containing dirt, salt, manure, and other materials. Solvent degreasing, usually performed only on sheepskins and pigskins, generates animal fat and waste skin material, spent detergents, and solvents. Unhairing is performed in an alkaline medium. The hair from the hair save method is usually disposed of in a landfill; however, the hair pulp process completely dissolves the hair. This process is the most significant source of proteinaceous organic and inorganic (lime) pollutants characterized by a high pH (10-12), and substantial amounts of BOD, TSS, sulfides, alkalinity, and nitrogen.

Best available demonstrated technology (BADT): It is the basis for establishing effluent limits for new industry sources as defined by Section 306 of the PL92-500 in the USA. BADT is described as those plant processes and control technologies that have demonstrated at a pilot plant level that technologically and economically they justify making investments in new production facilities.

Best available technology economically achievable (BATEA, or BAT): It is the highest degree of technology proved to be designable for plant-scale operation so that costs for this treatment may be higher than for treatment by best practicable technology (BPT), but economically achievable. BATEA, or BAT, is the treatment required by July 1, 1983 in the

USA for industrial discharge to surface waters as defined by Section 301 (b)(2)(A) of the PL92-500.

Best practicable control technology currently achievable (BPCTA, or BPT): It is a technology acceptable by the government taking into account such factors as age of equipment, facilities involved, process employed and process changes, engineering aspects of control techniques, and environmental impact apart from water quality, including energy requirements. In assessing BPT for a particular category of industry, a balance is struck between total cost and effluent reduction benefits. BPT is a treatment required by July 1, 1977 in the USA for industrial discharge to surface waters as defined by Section 301 (b)(1)(A) of the PL92-500.

Biochemical oxygen demand (BOD_5): The BOD_5 analysis, generally called BOD, is widely used to assess the environmental demands of wastewater. It should also be noted that, while BOD is a measure of the oxygen requirements of bacteria under controlled conditions, many effluent components take longer than the period of analysis to break down. Some chemicals will only be partially broken down, while others may not be significantly affected. Typically, vegetable tanning wastes have a long breakdown period, often quoted as being up to 20 days. These longer digestion periods can apply to a variety of chemicals used in manufacturing leather, including certain re-tanning agents, some synthetic fat liquors, dyes, and residual proteins from hair solubilization. This longer breakdown period means that the environmental impact is spread over a larger area as wastewater components are carried over greater distances before breaking down.

Chemical oxygen demand (COD): This method measures the oxygen required to oxidize the effluent sample entirely. It sets a value for the materials that would normally be digested in the BOD_5 analysis, the longer-term biodegradable products, as well as the chemicals that remain unaffected by bacterial activity. The semi-colloidal material in suspended solids is also included in the BOD and COD determinations. Normally 1 mg/L of suspended solids will generate a COD increase of approximately 1.5 mg/L.

Chlorides (Cl^-): Chloride is introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, it is not affected by effluent treatment and nature, thus remaining as a burden on the environment. Considerable quantities of salt are produced by industry and levels can rapidly rise to the maximum level acceptable for drinking water. Increased salt content in groundwater, especially in areas of high industrial density, is now becoming a serious environmental hazard. Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdowns in cell structure. If the water is used for irrigation purposes, surface salinity increases through evaporation and crop yields fall. When flushed from the soil by rain, chlorides re-enter the eco-system and may ultimately end up in the groundwater.

Chrome 3^+ (Trivalent Chrome, Chrome III): Chromium is mainly found in waste from the chrome tanning process; it occurs as part of the re-tanning system and is displaced from leathers during re-tanning and dyeing processes. This chrome is discharged in soluble form; however, when mixed with tannery wastewaters from other processes (especially if proteins are present), the reaction is very rapid. Precipitates are formed, mainly protein-chrome, which add to sludge generation. Very fine colloids are also formed which are then stabilized by the chrome - in effect, the protein has been partially tanned. The components are thus highly resistant to biological breakdown, and the biological process in both surface waters and treatment plants is inhibited. Once successfully broken down, chromium hydroxide precipitates and persists in the ecosystem for an extended period of time. If chrome discharges are excessive, the chromium might remain in the solution. Even in low concentrations, it has a toxic effect upon daphnia, thus disrupting the food chain for fish life and possibly inhibiting photosynthesis.

Chrome 6^+ (Hexavalent Chrome, Chrome VI): Dichromates are toxic to fish life since they swiftly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative. However, tannery effluents are unlikely to contain chromium in this form.

Chromium Compounds: Metal compounds are not biodegradable. They can thus be regarded as long-term environmental features. Since they can also have accumulative properties, they are the subject of close attention. Two forms of chrome are associated with the tanning industry, and their properties are often confused: (a) Chrome 3^+ (trivalent chrome, chrome III); and (b) Chrome 6^+ (hexavalent chrome, chrome VI)

Clari-DAF: It is rectangular dissolved air flotation (DAF) clarifier commercially available from Xylem Water and Wastewater, Zelienople, PA 16063, USA.

Coagulant: A chemical (alum or iron salts) added to water to destabilize particles, allowing subsequent floc formation and removal by clarification (flotation or sedimentation) and/or filtration.

Coagulation: A process of destabilizing charges of suspended and colloidal particles in water by adding chemicals (coagulants). In coagulation process, positively charged chemicals are added to neutralize or destabilize these negative charges and allow the neutralized particles to accumulate and be removed by clarification (flotation or sedimentation) and/or filtration.

Collector: A device or system designed to collect filter backwash water , or other treatment unit.

Comminuting: It is a grinding or shredding operation for reducing the particle size of objects or debris in the influent wastewater. They are installed with a screen directly in the influent wastewater flow's channel, with the shredded particles returned to the flow downstream of the screen. The influent flow is channeled to and through these units. The debris is collected against the screen, or outside drum, and the teeth which penetrate this screen cut up the solids. When the solids are reduced to the size of the screen or drum openings, they pass through and on for additional downstream wastewater treatment. The barminutor is a comminuting device that incorporates revolving cutters that move up and down the upstream face of a bar screen, shredding and cutting whatever debris has accumulated against the screen. The screenings are transported to the cutting device, shredded and then allowed to fall back into the influent channel downstream of the bar screen.

Conventional biological wastewater treatment system: It normally includes (a) preliminary treatment units (i.e. screen, comminutor, grit chamber etc. for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary sedimentation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary biological treatment units (such as activated sludge aeration or equivalent plus secondary sedimentation clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e. filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards.

Conventional physicochemical wastewater treatment system: It normally includes (a) preliminary treatment units (i.e. screen, comminutor, grit chamber etc. for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary sedimentation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary physicochemical treatment units (such as chemical precipitation/coagulation or equivalent plus secondary sedimentation clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e. filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards. In the nitrification and denitrification steps, only tertiary sedimentation clarification will be used for solid-water separation.

Dissolved air flotation (DAF): It is one of dissolved gas flotation (DGF) processes when air is used for generation of gas bubbles. See dissolved gas flotation (DGF).

Dissolved air flotation-filtration (DAFF): It is a package plant including both dissolved air flotation and filtration, such as Sandfloat, developed by the Lenox Institute of Water Technology (LIWT), and manufactured by Krofta Engineering Corporation (KEC) and their associated companies around the world. The filtration portion of DAFF can be sand filtration, multiple-media filtration, or granular activated carbon (GAC) filtration.

Dissolved carbon dioxide flotation (DCDF): It is one of dissolved gas flotation (DGF) processes when carbon dioxide is totally or partially used for generation of gas bubbles. See dissolved gas flotation (DGF).

Dissolved carbon dioxide flotation (DCDF): It is one of dissolved gas flotation (DGF) processes when carbon dioxide is totally or partially used for generation of gas bubbles. See dissolved gas flotation (DGF).

Dissolved gas flotation (DGF): It is a process involving pressurization of gas at 25 to 95 psig for dissolving gas into water, and subsequent release of pressure (to one atm) under laminar flow hydraulic conditions for generating extremely fine gas bubbles (20-80 microns) which become attached to the impurities to be removed and rise to the water surface together. The impurities or pollutants to be removed are on the water surface are called float or scum which scooped off by sludge collection means. The clarified water is discharged from the flotation clarifier's bottom. The gas flow rate is about one percent of influent liquid flow rate. The attachment of gas bubbles to the impurities can be a result of physical entrapment, electrochemical attraction, surface adsorption, and/or gas stripping. The specific gravity of the bubble-impurity agglomerate is less than one, resulting in buoyancy or flotation (i.e. Save-All).

Filtration: It is usually a granular medial filtration process which involves the passage of wastewater or water through a bed of filter media with resulting deposition f suspended solids. Eventually the pressure drop across the bed becomes excessive or the ability of the bed to remove suspended solids is impaired. Cleaning is then necessary to restore operating head and effluent quality. The time in service between cleanings is termed the filter run time or run length. The head loss at which filtration is interrupted for cleaning is called the terminal head loss, and this head loss is maximized by the judicious choice of media sizes. Dual media filtration involves the use of both sand and anthracite as filter ,media, with anthracite being placed on top of the sand. Gravity filters operate by either using the available head from the previous treatment unit, or by pumping to a flow split box after which the wastewater flows by gravity to the filter cells. Pressure filters utilize pumping to increase the available head. A filter unit generally consists of a containing vessel, the filter media, structures to support the media, distribution and collection devices for filter influent, effluent, and backwash water flows, supplemental cleaning devices, ad necessary controls for flows, water levels and backwash sequencing. Backwash sequences can include air scour or surface wash steps. Backwash water can be stored separately or in chambers that are integral parts of the filter unit. Backwash water can be pumped through the unit or can be supplied through gravity head tanks. Filtration may also include granular activated carbon (GAC) filtration and pressure filtration.

Floc: Collections of smaller particles that have agglomerated together into larger, more separable (floatable or settleable particlks as result of the coagulation process.

Flocculation: A water treatment unit process followibg coagulation that uses gentle stirring to bring suspended particles together so they will form largr, more separable (floatable or settleable) floc.

Flocculator/flocculation: Flocculator is a process device to enhance the formation of floc in a water. Mixing energy can be provided by slow turning mechanical means or head loss. A unit process involving the use of flocculators is called flocculation.

Granular activated carbon adsorption: Granular activated carbon (GAC) is used in wastewater substances GAC systems generally consist of vessels in which the carbon is placed, forming a "filter" bed. These systems can also include carbon storage vessels and thermal regeneration facilities. Vessels are usually circular for pressure systems or rectangular for gravity flow systems. Once the carbon adsorptive capacity has been fully utilized, it must be disposed of or regenerated. Usually multiple carbon vessels are used to allow continuous operation. Columns can be operated in series or parallel modes. All vessels must be equipped with carbon removal and loading mechanisms to allow for the removal of spent carbon and the addition of new material. Flow can be either upward or downward through the carbon bed. Vessels are backwashed periodically. Surface wash and air scour systems can also be used as part of the backwash cycle. Small systems usually dispose of spent carbon or regenerate iit offsite. Systems above about 3 to 5 MGD (million gallons per day) usually provide on-site regeneration of carbon for economic reasons.

Grinding: It is a unit operation for reducing the particle size of objects or debris in the influent wastewater, also termed shredding or comminuting. These devices may be installed with a screen directly in the wastewater flow or separately out of the wastewater flow, with the shredded particles returned to the flow downstream of the screen. Only those shredding and grinding devices that are installed directly in the influent channel are termed comminuting devices.

Grit chamber: It is a grit removal device that is designed to allow the settling out of this material. Grit removal is an important process for several reasons: (1) to prevent cementing effects at the bottom of sludge digesters and primary clarification tanks; (2) to reduce the potential for clogging of pipes and sludge hoppers; (3) to protect moving mechanical equipment and pumps from unnecessary wear and abrasion; (4) to reduce accumulations of materials in aeration tanks and sludge digesters which would result in a loss of usable volume; and (5) to reduce accumulations at the bases of mechanical screens. There are two types of grit chambers. The velocity controlled grit chambers limit the velocity in the rectangular channels to a maximum of 1 foot per second (fps). This velocity is low enough to allow the grit to settle but fast enough to maintain a majority of the organic material in suspension. The aerated grit chambers are normally sized on the basis of both detention time and volume of air. Typically, the detention time is in the range of 2 to 5 minutes and the air flow is in the range of 0.04 to 0.06 cu ft/ gallon of wastewater. The constant head type of system is normally designed using an overflow rate of 15,000 gallons per day per square foot and a 1 minute detention time at peak day flows.

Grit: It includes sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, and other large-sized unwanted materials in wastewater.

Gross Solids: Gross solids are larger than those a sampling machine can handle; hence they are not measured. Their presence, however, is clear to see and the dangers they pose are fully recognized. The waste components that give rise to this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags. They can be easily removed by means of coarse bar screens set in the wastewater flow. However, if they emerge from the factory, they settle out very rapidly. Major problems can develop if these materials settle in the pipes since they lead to blockages. The problems can be very serious when blockages occur in inaccessible piping. The cost of replacing burned-out motors or broken rotors is high. If discharged into gullies, ditches or water courses, the debris rapidly accumulates causing blockages and leading to stagnation.

Independent physicochemical wastewater treatment system (IPCWWTS): An Independent Physicochemical Wastewater Treatment System (IPCWWTS) utilizes physicochemical (PC) process technology other than biological process technology to obtain combined primary and secondary treatment efficiency for removals of mainly biochemical oxidation demand (BOD), chemical oxidation demand (COD), total suspended solids (TSS), and phosphate. Typically, an IPCWWTS uses combinations of preliminary treatment (flow equalization, bar screening, comminution, grit chamber, ammonia stripping), chemical precipitation/coagulation, primary clarification (primary sedimentation clarification or primary flotation clarification), secondary clarification (secondary sedimentation clarification, or secondary flotation clarification, without biological treatment), tertiary wastewater treatment (filtration, and/or granular activated carbon adsorption, ion exchange, PC oxidation, etc.), and disinfection. An innovative efficient primary flotation clarifier or a secondary flotation clarifier can be in any shape, circular or rectangular. In general this IPCWWTS requires much less land area than conventional biological secondary treatment systems. Phosphors removal is inherent in this physicochemical process system.

Innovative biological wastewater treatment system: It normally includes (a) preliminary treatment units (i.e. screen, comminutor, grit chamber etc. for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary flotation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary biological treatment units (such as activated sludge aeration or equivalent plus secondary flotation clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e. filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards.

Innovative physicochemical flotation wastewater treatment system: It includes (a) preliminary treatment units (i.e. screen, comminutor, grit chamber etc. for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary flotation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary physicochemical treatment units (such as chemical precipitation/coagulation or equivalent plus secondary flotation clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e. filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards. In the nitrification and denitrification steps, only tertiary flotation clarification will be used for solid-water separation.

Innovative physicochemical flotation-membrane wastewater treatment system: It includes (a) preliminary treatment units (i.e. screen, comminutor, grit chamber etc. for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary flotation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary physicochemical treatment units (such as chemical precipitation/coagulation or equivalent plus secondary membrane clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e. filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards. In the nitrification and denitrification steps, only tertiary membrane clarification will be used for solid-water separation.

KAMET: It is the abbreviation of Krofta Advanced Municipal Effluent Treatment (KAMET), and is a circular package plant consisting of both Supracell and Sandfloat with Supracell on the top. KAMET can be used for either water treatment or wastewater treatment, but is advertised for wastewater treatment.

KAMWT: It is the abbreviation of Krofta Advanced Municipal Water Treatment (KAMWT), and is a circular package plant consisting of both Supracell and Sandfloat with Supracell on the top. KAMWT can be used for either water treatment or wastewater treatment, but is advertised for water treatment.

Leather manufacturing: It is the inner layer of an animal skin, which consists primarily of the protein collagen, that is made into leather. Tanning is the reaction of the collagen fibers with tannins, chromium, alum, or other tanning agents to help stabilize or preserve the skin to make it useful.

Leather tanning or finishing: It is the conversion process of animal hides or skins into leather. Cattlehides, sheepskins, and pigskins are the major hides and skins used most often to manufacture leather.. To a lesser extent, hides and skins of horses, goats, deer, elk, calves, and other animals are also tanned. It is the inner layer of an animal skin, which consists primarily of the protein collagen, that is made into leather. Tanning is the reaction of the collagen fibers with tannins, chromium, alum, or other tanning agents to help stabilize or preserve the skin to make it useful. There are three major groups of subprocesses required to make finished leather: (a) Beamhouse oper¬ations; (b) tanyard processes; and (c) retanning and finishing processes. These processes and types of wastewater generated are described in the subsequent sections.

Method detection limit (MDL): It is defined as the minimum concentration of a substance that can be identified, measured and reported with 99 percent confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte.

Neutral Salts: Two common types of salts are to be found in tannery effluent: (a) sulphates and (b) chlorides.

Nitrification: It is a biological process by which ammonia in wastewater is converted by Nitrosomonas and Nitrobacter to nitrite, then to nitrate in the presence of oxygen. The biological reactions involved in these conversions may take place during activated sludge treatment, or a s separate stage following removal of carbonaceous materials. Separate stage nitrification may be accomplished via suspended growth or attached growth unit processes. In either case, the nitrification step is preceded by a pretreatment sequence (i.e. preliminary treatment, primary treatment, and secondary treatment). Possible secondary treatment may be (a) biological secondary treatment, such as activated sludge, trickling filter, roughing filter, plus secondary clarification; or (b) physicochemical secondary treatment, such as chemical precipitation/coagulation plus secondary clarification. Low BOD (i.e. BOD5/TKN ratio of less than 3) in the secondary effluent will assure a high concentration of nitrifiers (Nitrosomonas and Nitrobacter) in the nitrification biomass. The most common separate stage nitrification process is the plug flow suspended growth configuration with clarification. In this process, pretreatment effluent (i.e. nitrification influent) is pH adjusted as required, and aerated, in a plug flow mode. Because the carbonaceous demand is low, nitrifiers predominate. A clarifier (either sedimentation clarifier or flotation clarifier) follows aeration, and nitrification sludge is returned to the aeration tank. A possible modification is the use of pure oxygen in place of conventional aeration during the plug flow operation.

Nitrogen: Nitrogen is contained in several tannery effluent components. Sometimes, these sources have to be differentiated.

Oils and Grease: In leather manufacture, natural oils and grease are released from within the skin structure. If fat liquor exhaustion is poor, some fatty substances may be produced through inter-reaction when wastewaters mingle. Floating grease and fatty particles agglomerate to form "mats," which then bind other materials, thus causing a potential blockage problem especially in effluent treatment systems. If the surface waters are contaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is reduced. If these fatty substances emulgate, they create a very high oxygen demand on account of their bio-degradability.

Oxygen demand: Many effluent components are broken down by bacterial action into simpler components. Oxygen is required for both the survival of these (aerobic) bacteria and the breakdown of the components. Depending on effluent composition, this breakdown can be quite rapid or may take a very long time. If effluent with a high oxygen demand is discharged directly into surface water, the sensitive balance maintained in the water becomes overloaded. Oxygen is stripped from the water causing oxygen dependent plants, bacteria, fish - as well as the river or stream itself - to die. The outcome is an environment populated by anaerobic bacteria (which are not oxygen-dependent) leading to toxic water conditions. A healthy river can tolerate substances with low levels of oxygen demand. The load created by tanneries, however, is often excessive, and the effluent requires treatment prior to discharge. In order to assess the impact of effluent discharge on surface waters or determine the cost of treatment, oxygen demand needs to be determined.

pH value: Acceptable limits for the discharge of wastewaters into both surface waters and sewers vary, ranging from pH 5.5 to pH 10.0. Although stricter limits are often set, greater tolerance is shown towards higher pH values since carbon dioxide from the atmosphere or from biological processes in healthy surface water systems tends to lower pH levels very effectively to neutral conditions. If the surface water pH shifts too far either way from the pH range of 6.5-7.5, sensitive fish and plant life may be lost. Municipal and common treatment plants prefer discharges to be more alkaline to reduce the corrosive effect on concrete. Metals tend to remain insoluble and more inert, and hydrogen sulphide evolution is minimized. When biological processes are included in the treatment, the pH is lowered to more neutral conditions by carbon dioxide.

Preliminary effluent: The effluent from a preliminary treatment system (i.e. bar screen, comminutor, and grit chamber) by which most of large objects, such as rocks, logs and cans, grit, etc. in raw wastewater have been removed.

Preliminary treatment: It is the first treatment step, or preliminary step of either a conventional wastewater treatment system or an independent physicochemical treatment system. Preliminary treatment consists of bar screen, comminutor, and grit chamber mainly for removing large objects, such as rocks, logs and cans, grit, etc. from raw wastewater. Comminutor is an option depending on the nature and characteristics of raw wastewater.

Primary effluent: The effluent from a primary treatment system (either primary sedimentation clarification or primary flotation clarification) by which most of total suspended solids in wastewater have been removed.

Primary flotation clarification: It is a unit process or unit operation for removal of mainly total suspended solids (settleable solids and floatable solids) from screened wastewater using a primary flotation clarifier.

Primary flotation clarifier: A dissolved air flotation (DAF) reactor is used to float total suspended solids (TSS) from screened wastewater by decreasing their apparent density. DAF consists of saturating a portion or all of the wastewater feed, or a portion of recycled effluent with air at a pressure of 25 to 90 lb/square inch (gage). The pressurized wastewater is held at this pressure for 0.5 to 3 minutes in a retention tank and then released to atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to TSS and oil particles in the wastewater in the flotation chamber. This results in agglomeration which, due to the entrained air, have greatly increased vertical rise rates of about 0.5 to 2 ft/min. The floated materials rise to the surface to form a froth layer (float). Specially designed scrapers or other skimming devices continuously remove the froth (or float) . The retention time in the flotation chambers is usually about 20-60 minutes for rectangular flotation clarifier, and about 3-15 minutes for circular flotation clarifier using zero-horizontal velocity design. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended solids and/or oil which are to be removed from the waste stream. The attraction between the air bubble and particle is primarily a result of the particle surface charge and bubble-size distribution. The more uniform the distribution of water and micro-bubbles, the shallower the flotation clarifier can be. Generally, the depth of effective flotation units is between 3 and 9 feet.

Primary sedimentation clarification: It is a unit process or unit operation for removal of mainly total suspended solids (settleable solids and floatable solids) from screened wastewater using a primary sedimentation clarifier.

Primary sedimentation clarifier: It is a tank used to settle mainly total suspended solids (TSS) from screened raw wastewater by gravity. The main objectives of a primary sedimentation clarifier are removal of settleable solids by settling them to the clarifier bottom, and removal of floatable solids by skimming them from the clarifier's wastewater surface. In a rectangular sedimentation clarifier, the wastewater flows from one end to the other and the settled sludge is moved to a hopper at on end, either by scrapers called "flights" set on parallel chains, or by a single bottom scraper set on a traveling bridge. Floating materials,, such as grease and oil, are collected by a surface skimmer and then removed from the rectangular sedimentation clarifier. In a circular sedimentation clarifier, the wastewater usually enters in the middle and flows toward the outside edge. Settled sludge is pushed to the hopper that is in the middle of the circular clarifier's tank bottom. Floating material is removed by a surface skimmer connected to the sludge collector.

Primary treatment: It is an important wastewater treatment step (either primary sedimentation clarification or primary flotation clarification mainly for removing total suspended solids from preliminary treatment effluent) after the preliminary treatment (i.e. bar screen, comminutor, and grit chamber mainly for removing large objects from raw wastewater), but before secondary treatment (either biological treatment or physicochemical treatment mainly for removing dissolved organic/inorganic pollutants from primary effluent).

Rapid mixing: A water treatment unit process of quickly mixing a chemical solution uniformly through the process water.

Retanning and wet finishing processes: These are the final process steps after beamhouse operations and tanyard processes that give the tanned hide special desired characteristics. The final process steps used include: (a) retanning, (b) bleaching, (c) coloring, and fatliquoring, and (d) finishing. Retanning is used to give the leather certain special characteristics (different degrees of flexibility) which are lacking after the initial tanning step. The most common retanning agents are chromium, vegetable extracts (used to minimize variation between different parts of the chromium tanned hide), and syntans (used for softer side leathers and in making white or pastel leathers). In the sole leather industry, sodium bicarbonate and sulfuric acid are used to bleach the leather after tanning. Coloring involves combining dyes (usually aniline based) with the tanned skin fibers to form an insoluble compound. Dyes are added in the retanning wheels. Animal or vegetable fatliquors are added to replace the natural oils lost in the beamhouse and tanyard processes. Finishing includes all operations performed on the hide after fatliquoring, and includes finishing to enhance color and resistance to stains and abrasions, smoothing and stretching the s.kin, drying, conditioning, staking, dry milling, buffing, and plating. These processes generate wastes with additional quantities of tri-valent chromium, tannins, sulfonated oils, and spent dyes, which are low in BOD and TSS, high in COD, and at elevated temperature.

Sandfloat: It is combined circular dissolved air flotation and filtration (DAFF) clarifier invented and designed by the Lenox Institute of Water Technology (LIWT) and initially manufactured by Krofta Engineering Corporation (KEC).

Secondary effluent: The effluent from a secondary treatment step which may be either (a) biological treatment, such as activated sludge aeration or equivalent plus secondary clarification; or (b) physicochemical treatment, such as chemical precipitation/coagulation plus secondary clarification. Secondary treatment step removes most of dissolved organic/inorganic pollutants from primary effluent. Since secondary clarification (either secondary sedimentation clarification or secondary flotation clarification) is the final step of secondary treatment, the secondary effluent is also the secondary clarification effluent.

Secondary flotation clarification: It is a unit process or unit operation for removal of the bio-oxidation process generated activated sludge, and/or the chemical precipitation/coagulation process generated chemical sludge using a secondary flotation clarifier.

Secondary flotation clarifier: A dissolved air flotation (DAF) reactor is used to float biological sludge (activated sludge) from biologically oxidized wastewater (such as aeration tank effluent) and/or and/or chemical sludge from chemically coagulated /flocculated wastewater (such as flocculator effluent) by decreasing the sludge's apparent density. DAF consists of saturating a portion or all of the wastewater feed, or a portion of recycled effluent with air at a pressure of 25 to 90 lb/square inch (gage). The pressurized wastewater is held at this pressure for 0.5 to 3 minutes in a retention tank and then released to atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to suspended solids and other particles in the wastewater in the flotation chamber. This results in agglomeration which, due to the entrained air, have greatly increased vertical rise rates of about 0.5 to 2 ft/min. The floated materials rise to the surface to form a froth layer (float). Specially designed scrapers or other skimming devices continuously remove the froth (or float) . The retention time in the flotation chambers is usually about 20-60 minutes for rectangular flotation clarifier, and about 3-15 minutes for circular flotation clarifier using zero-horizontal velocity design. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended solids which are to be removed from the waste stream. The attraction between the air bubble and particle is primarily a result of the particle surface charge and bubble-size distribution. The more uniform the distribution of water and micro-bubbles, the shallower the flotation clarifier can be. Generally, the depth of effective flotation units is between 3 and 9 feet.

Secondary membrane clarification: A water-solid separation/clarification process uses membrane device instead of conventional sedimentation clarification in the secondary wastewater treatment step.

Secondary sedimentation clarification: It is a unit process or unit operation for removal of the bio-oxidation process generated activated sludge, and/or the chemical precipitation/coagulation process generated chemical sludge using a secondary sedimentation clarifier.

Secondary sedimentation clarifier: It is a tank used to settle the chemical precipitation/coagulation process generated chemical sludge, and/or the bio-oxidation process generated activated sludge for removing dissolved organic/inorganic substances from wastewater. The main objectives of a secondary sedimentation clarifier are removal of settleable chemical and/or biological sludge solids by settling them to the clarifier bottom. In a rectangular sedimentation clarifier, the wastewater flows from one end to the other and the settled sludge is moved to a hopper at on end, either by scrapers called "flights" set on parallel chains, or by a single bottom scraper set on a traveling bridge. In a circular sedimentation clarifier, the wastewater usually enters in the middle and flows toward the outside edge. Settled sludge is pushed to the hopper that is in the middle of the circular clarifier's tank bottom.

Secondary treatment: It is a wastewater treatment step after primary treatment (either primary sedimentation clarification or primary flotation clarification). Secondary treatment may be either biological treatment (such as activated sludge aeration plus secondary clarification) or physicochemical treatment (such as chemical precipitation/coagulation plus secondary clarification) mainly for removing up to 90 percent of dissolved organic pollutants from primary effluent.

Semi-Colloidal Solids: Semi-colloidal solids are very fine solids that, for all practical purposes, will not settle out even if the effluent is left to stand for a considerable period of time. Semi-colloidal solids will not directly cause a sludge problem. They can be broken down over an extended period by bacterial digestion and produce solids, which will eventually settle.

Settleable Solids (Solids With A Rapid Settling Rate): If wastewaters are to be treated in sewage works or to undergo traditional effluent treatment, the main problems that arise are due to the large volume of sludge that forms as the solids settle. Sludge often contains up to 97% water, giving rise to huge quantities of "light" sludge. Even viscous sludge has a water content of about 93% and can easily block sumps, sludge pumps and pipes. All this sludge has to be removed, transported, dewatered, dried and deposited, thus placing an inordinate strain on plant, equipment and resources. Even a thin layer of settled sludge can become a blanket that deprives sections of the river or lake bed of oxygen. As a result, aquatic life dies and decomposition sets in.

Shredding: It is a unit operation for reducing the particle size of objects or debris in the influent wastewater, also termed grinding or comminuting. These devices may be installed with a screen directly in the wastewater flow or separately out of the wastewater flow, with the shredded particles returned to the flow downstream of the screen. Only those shredding and grinding devices that are installed directly in the influent channel are termed comminuting devices.

Subcategory 1 (Leather Tanning Industry) Hair Pulp/Chrome Tan/Retan-Wet Finish: These are the tannery facilities which primarily process raw or cured cattle or cattle-like hides into finished leather by chemically dissolving the hair (hair pulp), tanning with trivalent chromium, and retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers, garments, upholstery, gloves, and lining material.

Subcategory 2 (Leather Tanning Industry) Hair Save/Chrome Tan/Retan-Wet Finish: These are the tannery facilities which primarily process raw or cured cattle or cattle-like hides into finished leather by chemically loosening and mechanically removing the hair (hair save), tanning with trivalent chromium, and retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers, handbags, garments, and gloves.

Subcategory 3 (Leather Tanning Industry) Hair Save or Pulp/Non-Chrome Retan/Retan-Wet Finish: These are the tannery facilities which process raw or cured cattle or cattle-like hides into finished leather by chemically dissolving (hair pulp), or loosening and mechanically removing the hair (hair save); tanning primarily with vegetable tannins, although other chemicals such as alum, syntans, or oils may be used; and retanning and wet finishing. Primary uses for the final products of this subcategory include sole leather, laces, harnesses, saddle leather, mechanical strap and skirting leather, and sporting good leathers (basketballs, footballs, softballs, baseballs, etc).

Subcategory 4 (Leather Tanning Industry) Retan/Wet Finish (Sides): These are the tannery facilities which process previously unhaired and tanned “wet blue" grain sides into finished'leather through retanning with trivalent chromium, syntans, vegetable tannins, or other tanning agents, coloring with dyes, and wet finishing processes including fatliquoring, drying (especially pasting frame or vacuum), and mechanical conditioning. Primary uses for the final products of this subcategory include shoe uppers, garments, and personal goods.

Subcategory 5 (Leather Tanning Industry) No Beamhouse: These are the tannery facilities which process previously unhaired and pickled cattlehides, sheepskins, or pigskins into finished leather by tanning with trivalent chromium or other agents, then retanning and wet finishing. Primary uses for the final products of this subcategory include garments, shoe uppers, gloves, and lining material.

Subcategory 6 (Leather Tanning Industry) Through-the-Blue: These are the tannery facilities which process raw or cured cattle or cattle-like hides only through the "wet-blue" tanned state by chemically dissolving or loosening the hair and tanning with trivalent chromium. No retanning or wet finishing is performed. The "wet blue" stock produced by this subcategory is subjected to further processing by plants in Subcategory 4 (grain sides) and plants in Subcategory 9 (splits).

Subcategory 7 (Leather Tanning Industry) Shearling: These are the tannery facilities which process raw or cured sheep or sheep-like skins with hair intact into finished leather by tanning with trivalent chromium or other agents, retanning, and wet finishing. Primary uses for hair on sheepskins (shearling) include hospital products, wool lined suede coats and similar garments, or specialty footwear, and seat covers.

Subcategory 8 (Leather Tanning Industry) Pigskin: These are the tannery facilities which process raw or cured pigskins into finished leather by chemically dissolving the hair and tanning with tri valent chromium, then retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers and gloves.

Subcategory 9 (Leather Tanning Industry) Retan/Wet Finish (Splits): These are the tannery facilities which process previously unhaired and tanned splits into finished leather through retanning and wet finishing processes that include coloring, fatliquoring, and mechanical conditioning. Primary uses for the final products of this subcategory include sueded leathers for garments, shoe uppers, and other specialty or personal goods.

Sulphates $(SO_4)^{2-}$: Sulphates are a component of tannery effluent which emanates from the use of sulphuric acid or products with a high (sodium) sulphate content. Many auxiliary chemicals contain sodium sulphate as a by-product of their manufacture. For example, chrome tanning powders contain high levels of sodium sulphate, as do many synthetic re-tanning agents. Removing the sulphide component from effluent by aeration creates an additional source, since the oxidation process produces a whole range of substances, including sodium sulphate. Sulphates can be precipitated by calcium-containing compounds to form calcium sulphate that has a low level of solubility. Problems arise with soluble sulphates, however, for two main reasons: **(a)** Sulphates cannot be removed completely from a solution by chemical means. Under certain biological conditions, it is possible to remove sulphate from a solution and bind the sulphur into micro-organisms. Generally, however, the sulphate either remains as sulphate or is broken down by anaerobic bacteria to produce malodorous hydrogen sulphide. This process occurs very rapidly in effluent treatment plants, sewage systems and water courses, if effluents remain static. This bacterial conversion to hydrogen sulphide in sewage systems results in the corrosion of metal parts, and unless it is sulphate-resistant, concrete will gradually erode. **(b)** If no breakdown occurs, there is the risk of increasing the total concentration of salts in surface waters and groundwater.

Sulphides (S^{2-}) : The sulphide content in tannery effluent results from the use of sodium sulphide and sodium hydrosulphide and the breakdown of hair in the unhairing process. Sulphides pose many problems. Under alkaline conditions, sulphides remain largely in solution. When the pH of the effluent drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH, the higher the rate of evolution. Characterized by a smell of rotten eggs, a severe odour problem occurs. In its toxicity, hydrogen sulphide is comparable to hydrogen cyanide; even a low level of exposure to the gas induces headaches and nausea, as well as possible eye damage. At higher levels, death can rapidly set in, and countless deaths attributable to the build-up of sulphide in sewage systems have been recorded. Hydrogen sulphide gas is also soluble. When absorbed, weak acids can form and cause corrosion. This weakens metal roofing, girders and building supports. In sewers, major problems can arise as metal fittings, structural reinforcements and piping corrode. If discharged into surface water, even low concentrations pose toxic hazards. Sulphides can be oxidized into non-toxic compounds by certain bacteria in rivers; however, this creates oxygen demand that, if excessive, can harm aquatic life.

Supracell: It is a circular dissolved air flotation (DAF) clarifier initially invented and designed by the Lenox Institute of Water Technology (LIWT) and subsequently manufactured by Krofta Engineering Corporation (KEC) and its associated companies around the world.

Suspended Solids: Suspended solids present in effluents are defined as the quantity of insoluble matter contained in the wastewater. These insoluble materials cause a variety of problems when discharged; essentially, there are two types of solids distinguished by significantly different characteristics.

Tannery: The facilities that perform leather tanning or finishing operations are tanneries. In general, most tanneries perform the entire tanning process, from beamhouse to tanyard , then to wet finishing operations. A smaller number perform only beamhouse and tanyard operations and sell their unfinished product (wet "blue" stock) to other tanneries to produce specific leathers. There are nine subcategories of tanneries which have been identified based on distinct combinations of raw materials and leather processing operations. See Subcategories 1 to 9.

Tanyard processes: They follow the beamhouse operations and consist of bating, pickling, tanning, wringing, splitting, and shaving. Bating involves the addition of salts of ammonium sulfate or ammonium chloride used to convert the residual alkaline chemicals present from the unhairing process into soluble compounds which can be washed from the hides or skins. The addition of bates, enzymes similar to those found in the digestive systems of animals', facilitate the separation of the collagen protein fibers and destroy most of the remaining undesirable constituents of the hide, such as hair roots and pigments. Pickling prepares the hides to accept the tanning agents (i.e., chrome) usually by adding sulfuric acid to provide the acid environment necessary for chromium tanning. In the tanning process, tanning agents such as trivalent chromium, vegetable tannins, alum, syntans, formaldehyde, gluteraldehyde, and heavy oils, convert the raw collagen fibers of the hide into a stable product no' longer susceptible to putrefaction or decomposition. They also improve the dimensional stability, resistance to heat, chemicals and abrasion, and flexibility of the raw materials. Vegetable tanning is used in the production of heavy leathers such as sole leather and saddle leather. Chromium tanning is usually preferred by the majority of leather users, i.e., shoe and garment manufacturers. Blue hides (hides after beamhouse and tanyard operations) are wrung to remove excess moisture through a machine similar to a clothes wringer. Splitting adjusts the thickness of the tanned hide to the requirements of the finished product and produces a split ("drop") from the flesh side of the hide. These splits may or may not be retanned and wet finished at the same facility. Shaving removes any remaining fleshy matter from the flesh portion of the hide. Wastewater from tanyard operations contain.inorganic chemical salts, small amounts of proteinaceous hair and waste, and large amounts of ammonia from the bating process. Pickling generates a highly acidic waste (pH of 2.5-3.5) which contains salt. Spent chromium liquors contain high concentrations of tri-valent chromium in acid solution with low concentrations of BOD and TSS and elevated temperatures. Discharges, (blowdown) from vegetable tanning vats necessary to maintain vegetable tanning liquor quality is highly colored and contains significant amounts of BOD, COD, and dissolved solids.

Total Kjeldahl Nitrogen (TKN): Several tannery effluent components contain nitrogen as part of their chemical structure. The most common chemicals are ammonia (from deliming materials) and the nitrogen contained in proteinaceous materials (from liming/unhairing operations). These sources of nitrogen pose two direct problems: (a) Plants require nitrogen in order to grow, but the high levels released by substances containing nitrogen over-stimulate growth. Water-based plants and algae grow too rapidly, whereupon waterways become clogged and their flow is impaired. As the plants die, a disproportionately high amount of organic matter has to be broken down. If the load outstrips the natural supply of oxygen from the river, plants, fish and aerobic bacteria die and ultimately anaerobic conditions develop. **(b)** The nitrogen released through protein breakdown and the deliming process is in the form of ammonia. Bacteria can convert the latter over several stages into water and nitrogen gas, which is ultimately released into the atmosphere. Both of these breakdown products are non-toxic, yet large amounts of oxygen are needed in the process. If oxygen demand is greater than the level supplied naturally by the body of water, toxic anaerobic conditions can rapidly develop. Combining intensive aerobic and anoxic biological treatment can break down the nitrogenous compounds. The oxygen demand is very high, thus leading to correspondingly high operational and energy costs. Calculations show that, with typical tannery effluent, some 40% of oxygen requirements are spent on removing the nitrogen component.

United Nations Industrial Development Organization (UNIDO): It is a specialized agency of the United Nations (UN) with about 170 member states. The member states regularly discuss and decide UNIDO’s guiding principles and policies in their sessions of the policymaking organs. The UNIDO's mission is to promote a new humanity science of industrial ecology (IE) and accelerate inclusive and sustainable industrial development (ISID) in member states. Natural resources recovery, environmental sustainability, and proper management solid, liquid and gaseous wastes are emphasized within ISID. The UNIDO's programmatic focus is structured, as detailed in the UNIDO's Medium-Term Program Framework 2018-2021, in four strategic priorities: (a) creating shared prosperity; (b) advancing economic competitiveness; (c) safeguarding the environment; and Strengthening knowledge and institutions. Since UNIDO is mainly assisting developing countries, so some industrialized countries which are the UN member states have refused to pay the UNIDO membership fees becoming the UNIDO member states.

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Appendix A. Discharge Limits for Treated Tannery Effluents in France, Italy and India (Source: UNIDO) [35]

Parameter	Unit	France		Italy		India	
		Surface	Sewer	Surface	Sewer	Surface	Sewer
pH	–	6.5-8.5	6.5-8.5	5.5-9.5	5.5-9.5	5.5-9.0	5.5-9.0
COD	mg/l	125	2000	160	500	250	–
BOD_5	mg/l	30	800	40	250	30	350
Suspended solids	mg/l	35	600	40-80	200	100	100
Ammonia nitrogen (as NH_4)	mg/l	–		15	30	50	50
TKN	mg/l					100	
Nitrate nitrogen (as N)	mg/l	–		20		–	
Total nitrogen in sensitive areas	mg/l	30 15	150			–	
Sulphide (S^{2-})	mg/l			1	2	2	–
Hexavalent chromium, Cr^{6+}	mg/l	0.1	0.1	0.2	0.2	0.10	2.0
Trivalent chromium, Cr^{3+}	mg/l	1.5	1.5	-	4.0	–	–
Total chrome (as Cr)	mg/l	–		2.0	4.0	2	2
Iron + aluminium	mg/l	5	5			–	
Phenol index	mg/l	0.3				1[1]	5[1]
AOX	mg/l	1.0	1.0			–	
Chlorides (as Cl^-)	mg/l	***		1200*	1200	**	**
Sulphates (as SO_4^{2-})	mg/l	***		1000*	1000	1000	1000
Aluminium (as Al)	mg/l	–	–	1.0	2.0	–	–
Iron (as Fe)	mg/l	–	–	2.0	4.0	–	–

[1] As phenolic compounds (as C_6H_5OH).

* Special limits permitted by the regional authorities to certain CETPs located close to the sea or if the effluent is mixed with sanitary wastewater:

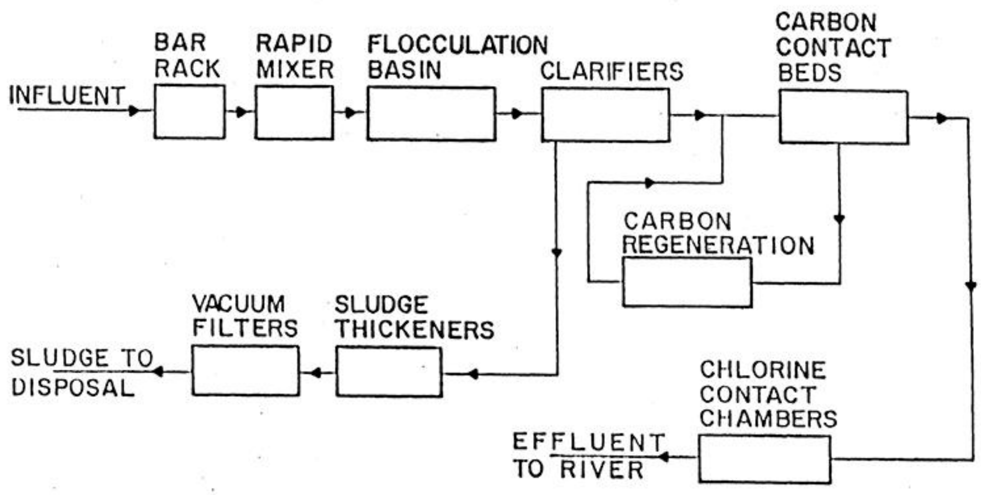
- at Santa Croce, CuoioDepur and Fuccechino – chlorides: 5,000 mg/l; sulphates: 1,800 mg/l;
- at Arzignano – chlorides: 900 mg/l; sulphates: 1,800 mg/l;
- at Solofra – chlorides: 3,500 mg/l; sulphates: 1,500 mg/l.

** In Tamil Nadu, India – TDS limit: 2,100 mg/l; chlorides: 1,000 mg/l; sulphates: 1,000 mg/l, for discharge in surface water and sewer. Previously, up to 7,500 mg/l TDS were tolerated by the authorities.

*** In France, no discharge limits pertaining to chlorides, sulphates and TDS have been prescribed except in special cases. (The authorities do not insist on norms relating to COD and nitrogen, if the effluent is treated alongside with domestic sewage in a combined treatment plant. This relates exclusively to effluent discharged in a sewer).

Note: The data in the table above refer to the year 2002.

Appendix B. Schematic of the City of Niagara Falls Wastewater Treatment Facility, Niagara Falls, NY, USA; An Independent Physicochemical Wastewater Treatment System (IPCWWTS) Treating 48-MGD Average Flow and 86-MGD Peak Flow Since 1976. Authors and Senior Managers of Niagara Falls IPCWWTS [15-17]



APPENDIX C

Editors of

"EVOLUTIONARY PROGRESS IN SCIENCE, TECHNOLOGY, ENGINEERING, ARTS AND MATHEMATICS (STEAM)"

1. Dr. Lawrence K. Wang (王抗曝)

Editor Lawrence K. Wang has served the society as a professor, inventor, chief engineer, chief editor and public servant (UN, USEPA, NY, Albany) for 50+ years, with experience in entire field of environmental science, technology, engineering, arts and mathematics (STEAM). He is a licensed NY-MA-NJ-PA-OH Professional Engineer, a certified NY-MA-RI Laboratory Director, a MA-NY Water Operator, and an OSHA Train-the-Trainer Instructor.

He has special passion, and expertise in developing various innovative technologies, educational programs, licensing courses, international projects, academic publications, and humanitarian organizations, all for his dream goal of promoting world peace. He is a retired Acting President/Professor of the Lenox Institute of Water Technology (LIWT), USA, a United Nations Industrial Development Organization (UNIDO) Senior Advisor in Vienna, Austria, and a former professor/visiting professor of Rensselaer Polytechnic Institute, Stevens Institute of Technology, University of Illinois, National Cheng Kung University, Zhejiang University, and Tongji University.

Dr. Wang is the author of 750+ papers and 60+ books, and is credited with 29 invention patents. He holds a BSCE degree from National Cheng Kung University, Taiwan, ROC, a MSCE degree from the University of Missouri, a MS degree from the University of Rhode Island and a PhD degree from Rutgers University, USA. Currently he is the book series editor of CRC Press, Springer Nature Switzerland, Lenox Institute Press, World Scientific Singapore, and John Wiley.

Dr. Wang has been a Delegate of the People to People International Foundation, an American Academy of Environmental Engineers (AAEE) Diplomate, a member of WEF, AWWA, ASCE, AIChE, ASPE, CIE and OCEESA, and a recipient of WEF Kenneth Research Award (NY), Five-Star Innovative Engineering Award (first DAF drinking water plant in Americas), and Korean Pollution Control Association Award (Transfer of flotation technology to South Korea).

2. Dr. Hung-ping Tsao (曹 恆 平)

Editor Hung-ping Tsao has been a mathematician, a university professor, and an assistant actuary, serving private firms and universities in the United States and Taiwan for 30+ years. Dr. Tsao has been an Associate Member of the Society of Actuaries and a Member of the American Mathematical Society.

His research have been in the areas of college mathematics, actuarial mathematics, management mathematics, classic number theory and Sudoku puzzle solving. In particular, bikini and open top problems are presented to share some intuitive insights and some type of optimization problems can be solved more efficiently and categorically by using the idea of the boundary being the marginal change of a well-rounded region with respect to its inradius; theory of interest, life contingency functions and pension funding are presented in more simplified and generalized fashions; the new way of the simplex method using cross-multiplication substantially simplified the process of finding the solutions of optimization problems; the generalization of triangular arrays of numbers from the natural sequence based to arithmetically progressive sequences based opens up the dimension of explorations; the introduction of an innovative way to solve Sudoku puzzles makes everybody's life so much easier and other STEAM project development.

Dr. Tsao is the author of 10+ books and over 40 academic publications. Among all of the above accomplishments, he is most proud of solving manually in the total of ten hours the hardest Sudoku posted online by Arto Inkala in early July of 2012 and introducing an easy way to play Sudoku in 2019.

He earned his high school diploma from the High School of National Taiwan Normal University, his BS and MS degrees from National Taiwan Normal University, Taipei, Taiwan, his second MS degree from the UWM in USA, and a PhD degree from the University of Illinois, USA.

Editors of the eBOOK Series of the *"EVOLUTIONARY PROGRESS IN SCIENCE, TECHNOLOGY, ENGINEERING, ARTS AND MATHEMATICS (STEAM)"*

Dr. Lawrence K. Wang (王抗曝) - - left

Dr. Hung-ping Tsao (曹恆平) -- right

APPENDIX D

THE E-BOOK SERIES OF

"EVOLUTIONARY PROGRESS IN SCIENCE,TECHNOLOGY, ENGINEERING,

ARTS AND MATHEMATICS (STEAM)"

The acronym STEM stands for “science, technology, engineering and mathematics”. In accordance with the National Science Teachers Association (NSTA), “A common definition of STEM education is an interdisciplinary approach to learning where rigorous academic concepts are coupled with real-world lessons as students apply science, technology, engineering, and mathematics in contexts that make connections between school, community, work, and the global enterprise enabling the development of STEM literacy and with it the ability to compete in the new economy”.

The problem of this country has been pointed out by the US Department of Education that “All young people should be prepared to think deeply and to think well so that they have the chance to become the innovators, educators, researchers, and leaders who can solve the most pressing challenges facing our nation and our world, both today and tomorrow. But, right now, not enough of our youth have access to quality STEM learning opportunities and too few students see these disciplines as springboards for their careers.” STEM learning and applications are very popular topics at present, and STEM related careers are in great demand.

According to the US Department of Education reports that the number of STEM jobs in the United States will grow by 14% from 2010 to 2020, which is much faster than the national average of 5-8 % across all job sectors. Computer programming and IT jobs top the list of the hardest to fill jobs.

Despite this, the most popular college majors are business, law, etc., not STEM related. For this reason, the US government has just extended a provision allowing foreign students that are earning degrees in STEM fields a seven month visa extension, now allowing them to stay for up to three years of “on the job training”. So, at present STEM is a legal term.

The acronym STEAM stands for “science, technology, engineering, arts and mathematics”. As one can see, STEAM (adds “arts”) is simply a variation of STEM. The word of “arts” means application, creation, ingenuity, and integration, for enhancing STEM inside, or exploring of STEM outside.

It may also mean that the word of “arts” connects all of the humanities through an idea that a person is looking for a solution to a very specific problem which comes out of the original inquiry process. STEAM is an academic term in the field of education. The University of San Diego and Concordia University offer a college degree with a STEAM focus.

Basically STEAM is a framework for teaching or R&D, which is customizable and functional, thence the “fun” in functional. As a typical example, if STEM represents a normal cell phone communication tower looking like a steel truss or concrete column, STEAM will be an artificial green tree with all devices hided, but still with all cell phone communication functions. This e-book series presents the recent evolutionary progress in STEAM with many innovative chapters contributed by academic and professional experts.