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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

CLEAN TECHNOLOGY DIGEST

(A PROPOSAL) *

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* This document has not been edited

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Preface

A "Digest" of industrial pollutants, sources and agents, and of clean technologies (CT) for a succ^ossful risk management, should be considered an integral part of any guidelines for the transfer of environmentally sound technologies for sustainable development.

The international attempts I.S.I.C. (Indexes to the International Standard Industrial Classification of all Economic Activities)⁽⁵¹⁾ arrives at the impressive number of 12,000 categories.

Even more stupendous is the list of known chemicals, namely seven million. Of these it is estimated 60,000 impact or the environment; however, only 1,000 have been studied in any detail in this respect.

Only recently has an economic view emerged that pollutants cause not only detrimental environmental effects, but also constitute often raw materials. Environmental degradation occurs, when real waste is simply discharged into air, water and soil and not recycled or reused. Frofit can come from wastes, when new and clean environmental technologies are used.

The international literature and information documenting this dynamic development and explosive growth is only beginning to be harnessed by data banks.⁽⁶¹⁾ It becomes evident that an on-going digest of this enormous volume of literature, especially for practitioners---workers, middle management and executives---in multifarious industrial and manufacturing enterprises, has become a dire necessity.

The following is submitted as an initial proposal for a systematic framework and select examples. The major purpose is to give some guidelines for a many-volumed digest in ring-note-book format with regularly updated editions. The present limitations were only set by the brevity of working time available, that is one man/month contract.

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The result had to be a selective exploration. The examples are to illustrate the necessity and feasibility of this approach for a digest.

The basic philosophy behind this approach is best circumscribed by the environment portions of the World Commission on Environment and Development known as <u>Our Common Future</u>, (67)

" the overriding policy objective must be to reduce the amount of waste generated and to transform an increasing amount through recycling into resources for reuse. "

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Introduction

This Introduction offers both a summary of the "Digest" and presents brief overviews of the issues.

The digest is to be a handy source for practical information. There are some basic informations which are not likely to change. However, the informations concerning the findings in and the application of CT are likely to change. Although this adds to the complication of the subject matter, it has been the aim to present issues simply and to refer the interested reader to additional sources of expert specialist opinions. Since the subject matter changes rapidly and dynamically, today's innovative experts may be tomorrow's conventional specialists. Add to this that the development of CT moves particularly fast. It is an innovative field. Practitioners might find themselves anywhere on this continuum of conventional ET to innovative CT. The Digest aims to be detailed enough for a reader to identify the current status of ET in his enterprise and the potential trends of future technological developments in CT.

PART I commences with the processes. It purports to identify major industrial production and manufacturing systems emitting various substances into air, soil and water. (For practical purposes of presentation, "soil" has not been included in this proposed first draft). At this time only several systems have been identified from the following larger, yet select and possible list.⁽⁵¹⁾ From an alphabetical list of more than 12,000 items, approximately 8,500 numeric index numbers exist. Each process system is henceforth idetified by its I.S.I.C. index number.

<u>Index No.</u>	Production Branch
2100	CCAL (mining)
2200	OIL (crude) and GAS (natural) (exploration)
2301	IRON ORE (mining)
2302	NON-FERROUS ORE (mining)
3111	SLAUGHTERING and MEA'1-PACKING (preparing and preserving)

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3112	DAIRY (products manufacturing)
3113	CANNERY (preserving fruits and vegetables)
3114	CANNERY (fish, crustacean and similar)
3115	RENDERING
3118	SUGAR (refining)
3131	DISTILLERY
3132	WINERY
3133	BREWERY
3211	TEXTILES (spinning, weaving, finishing)
3231	TANNERY (and leather finishing)
3411	PULP, PAPER, PAPERBOARD (manufacture)
3511	CHEMICALS (mrnufacture of basic industrial chemicals, except fertilizers)
3512	FERTILIZERS and PESTICIDES (manufacture)
3521	PAINTS, VARNISHES, LACQUERS (manufacture)
3522	PHARMACEUTICS (manufacture of drugs and medicines)
3530	PETROLEUM (refineries)
3540	PETROCHEMICALS (petrolgum and coal products manufacture
3551	RUBBER (tire and tube industry)
3560	PLASTIC (manufacture of plastic products not found elsewhere)
3692	CEMENT (manufacture; also of LIME and PLASTER)
3599	MINERAL PRODUCTS (non-metallic, not elsewhere classified)
3710	IRON (foundry) and STEEL (mills, basic industries)
3720	NON-FERROUS METALS (basic industries)
3819	PLATING (electro and chemical, except jewelry)
9520	LAUNDRY (services, cleaning and dyeing plants)

The above have also been chosen, in order to illustrate the kind of production branch, industrial and manufacturing activity, which contributes most to environmental deterioration in developing countries.

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Special care needs to be taken to commence selecting those processes which contribute in particular to the local risks; affecting local populations and being amenable to local communal environmental amelioration. CT in particularly useful for solving local problems.⁽⁵²⁾ From that stage the processes advance naturally to more complex systems. Pollution abatement and waste management in these become more complicated and more expensive. It is usually beyond the reach of communal populations. It becomes increasingly the responsibility of the next higher levels of government. The reader can observe the emissions from each part of the production process. The informed consumers will look differently at their living standard and the quality of life once cause and effects, intimately touching them, become more apparent.

In PART II we are concerned at this point with some major emissions. Few of the hazardous ones are among them. Chemical emissions are identified by formula and names. A longer list can be found at the beginning of PART II.

In PART III are presented some environmental technologies (ET). Evidently more conventional ones exist than new ones of CT. Science and industry have responded vigorously to the development of remedial end-pipe ET. Their growing application also proves the beneficial interrelationship between economics and ecology. Environmental concerns are economic concerns. The massive development of new sciences, like gene-technology for example, opens unheard of new possibilities also to CT. Preventive CT methods have a qualitative and quantitative future in environmental amelioration and in the reshaping of industrial processes. Again for both remedial and preventive ET selective examples, matching PART I, are offered.

A number of appendices help elaborate. APPENDIX A presents selected Data-Bases. APPENDIX B informs those searching for more detailed and more sophisticated information by means of a select Bibliography.

Any overview of the issues focuses on clean technologies (CT). Three questions are raised: CT, the economic argument; CT, the environmental amelioration argument; and CT, the human health argument.

The Digest points to a solution known as CT. CT refers to technologies designed specifically to prevent waste emissions at the source generation, rather than to treat them at the end of the production process.

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In this sense, reduced waste, along with energy and resource conservation, are integral to the very design of the industrial process and its attendant technology. Strategies may include product reformulation, substitution with less hazardous feedstock, installation of more efficient equipment, recycling technologies and the like. There is convincing evidence gathering that CT is the most economic way of reducing environmental pollution in comparison with conventional abatement techniques. Low-waste technologies of CT are turning out in practice to be among the best economic choices, since an industry can thereby obtain a higher output for a given input.

CT can be presented to serve many economic purposes:

- the reduction of pollution generated by conventional industrial processes
- the improvement of process efficiency and energy conservation, leading to more cost-effective and profitable industrial operations
- the optimization of the use of new materials, thereby promoting a more efficient use of natural resources
- the development of environmentally appropriate technologies.

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Not all ET are CT: As has been well pointed out recently (47) because of this difference new strategies for manufacturing are beginning to intrigue those for whom wastes from one industrial process can serve as the raw materials for another. This reduces the impact of industry on the environment which ought to become UNIDO's most sacred obligation after its General Conference in November 1989 has adopted the new Environment Programme. This is part of the future that has already happened.⁽¹²⁾ In the past sciences and technologies have overlapped very little. The major driving force behind business and trade has become lately the trend towards alliances. Sciences combine their efforts in bio-technology, for example. Technology and markets combine. In the past technology did not overlap with another. Electronics people did not need to know much about electrical engineering and about materials. Paper-makers needed to know mainly about paper mechanics and paper chemistry. CT is fostering alliances, because of the interdependence of constituent parts. Ecology elicits interdependence. Markets, similarly are rapidly changing, merging, criss-crossing and overlapping each other. All this is not easy. Clarity in respect to objectives, strategies, policies and goals are required. This is why, also, increasingly social scientists are concerned with ecology and technology.

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The following charts and tables are to elucidate the environmental amelioration argument.

TABLE 1, a matrix emisions from industrial sources (50, p.204) helps elcudiate the challenge. TABLE 2, the application of various processes in air pollution control (50, p.747) displays some of the answers to this challenge. The purification processes are both an example of the success of applied interdependence of science and technology, ecology and economics, as well as an indication of the numerous inventions of ET and CT in the field of purification processes.

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TABLE 1 (Matrix	of	Typical	Emicsions	from	Industrial	Sources)

Chapter Industrial	2	3	4	5	6/7	8	9	10	10	11	aste 12	
Sources	Mineral	=		ver	tal	Chemical	Forestry	po	Animal	Other	Comb./waste	
Substance	Σ.	Coal	Ö	Power	Mctal	ວົ	For	Food	٩		<u> </u>	
Particulates	x	x	х	х	Х	Х	X	X	X	х		
Sulfur oxides	х	х	х	Х	Х	Х	Х	X	X			
Nitrogen oxides	Х	x	х	х	Х	Х	X	Х	Х			
Carbon monoxide	Х	x	х	Х	X	х		Х			N	
Hydrocarbons	х	x	Х	Х		Х	X	Х	X	X X		•
Chlorin ated HCOs						Х			X	Л		,
mmonia compounds	х	X	Х			Х	Х	Х	Х		>	•
Ashestos	Х					Х						
Chlorine	x			X	Х	Х	Х			X		
Bromine						Х						
Fluorides	х			x	х	Х				X		
Hydrogen sulfide		х	х			Х	Х	Х	X		2	x
Acetic acid												
Hydrochloric acid						Ν		Х	Х			
		х				х				X		
Hydrogen cyanide Nitric acid						Х						
						х						
Phosphoric acid						х						
Sulfuric acid					х							
Aluminium	v				-							
Antimony	х					х						
Arsenic												
Beryllium				х					x			
Cadmium	••			x					х			
Chromium	X			~								
Copper	X					x						
Iron			N	v	v	~			x			
Lead	x		х	х		v			,.			
Magnesium	x				x	х						
Manganese						v						
Mercury				x		x						
Molybdenum												
Nickel			Х	x								
Selenium	х				_						x	
Silica	X				X						~	
Vanadium			Х	Х								
Zinc				Х		X						
Organics		x	Х			X		() X			X	.,
Amines						Х				X	X	X
Aldehydes			x	>	(X		C C	2	X	Х	х
Carbon disulfide		X	x			N						
Mercaptans		x				N	()	< ?	x	Х	х	x
Phthalic anhydride												
Toluene isocyanate						>						
Trichloroethylene						2				Х	х	
						>	Ś				Х	
Vinyl chloride					y							
Carbon black		N	,		•	-	•	X		x	Х	
Phenols						•			X	X	X	

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	Material and marginal condition	Purification processes	Industrial application
Inorganic gases	Sulfur dioxide	chemical absorption, adsorption with catalytic conversion	thermal power stations, in- dustrial boilers, incinerators, chemical plants, treatment of sulfur-containing gases
	Nitrogen oxide	oxidising alkali scrubbing, catalytic conversion	thermal power stations, in- dustrial boilers, plants for 'INO3 production
	Hydrochloric acid, hydrofluoric acid	absorption, adsorption	thermal power stations, brickworks, refuse incinera- tors
	Hydrogen sulfide (high concentration, secondary treatment)	chemical absorption, adsorption with catalytic oxidation	rayon production plants, coking plants, coal gasifica- tion plants, coal liquefaction plants, synthesis gas pro- duction plants, natural gas purification plants
	Radioactive gases	adsorption, isotopic exchange	nuclear power stations
Organic vapours and gases	High concentration (possible energy use)	catalytic or thermal secondary combustion	solvent recovery e.g. in fel- lowing plants: tape produc- tion, rayon production,
v	High concentration (water-soluble)	absorption in aqueous solution	printing machines, dry cleaning, production of plastics, coating with plastic
	Low concentration (recovery)	adsorption	films, metal degreasing, varnishing (e.g. of auto- mobiles), gasoline recovery
	Very low concentration (no recovery)	adsorption with second- ary combustion	from tanks

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TABLE 3 attempts to summarize some of the major liquid industrial wastes. (35, p.305) It serves for a quick overview.

TABLE 3 (Major Liquid Industrial Wastes)

Industries producing wastes	Origin of major wastes	Major characteristics	Major treatment and disposal methods
Textiles	Cooking of fibers, desizing of fabric	Highly alkaline, colored, high BOD and temperature, high suspended solids	Neutralization, chemical pre- cipitation, biological treatment, aeration and/or trickling filtration
Leather goods	Unhairing, soaking, deliming, and bating of hides	High total solids, hardness, salt, sulfides, chromium, pH, precipitated lime, and BOD	Equalization, sedimentation, and biological treatment
Laundry trades	Washing of fabrics	High turbidity, alkalinity, and organic solids	Screening, chemical precipita- tion, Rotation, and adsorption

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Industries pro- ducing wastes	Origin of major wastes	Major characteristics	Major treatment and disposal methods
Canned goods Trimming, culling, juicing, and blanching of fruits and vegetables		High in suspended solids, col- loidal and dissolved organic matter	Screening, lagooning, soil ab- sorption or spray irrigation
Dairy products	Dilutions of whole milk, sep- arated milk, buttermilk, and whey	High in dissolved organic mat- tel, mainly protein, fat, and lactose	Biological treatment, aeration, trickling filtration, activated sludge
Brewed and distilled beverage:	Steeping and pressing of grain, s residue from distillation of alcohol; condensate from stillage evaporation	High in dissolved organic solids, containing nitrogen and fer- mented starches or their products	Recovery, concentration by centrifugation and evaporation, irickling filtration, use in feeds digestion of slops
Metal container	Cutting and lubricating metals, cleaning can surface	Metal fines, lub. oils, variable pH, surfactants, dissolved metals	Oil separation, chemical precipi- tation, collection and reuse, lago- storage. Final carbon absorption
Petrochemicals	Contaminated water from chemical production and transportation of second generation oil compounds	High COD, T.D.S., metals, COD/BOD ratio, and cpds. in- hibitory to biol. action	Recovery and reuse, equaliza- tion and neutralization, chemical coagulation, settling or flotation, biological oxidation
Cement Fine and finish grinding of cement, dust leaching collection, dust control		Heated cooling water, suspended solids, some in- organic salts	Segregation of dust-contact streams, neutralization and sedimentation
Wood furniture	Wet spray booths and laundries	Organics from staining and sealing wood products	Evaporation or burning
Asbestos	Cleaning and crushing ore	Suspended asbestos and mineral solids	Detention in ponds, neutraliza- tion and land filling
Paint and inks	Solvent-based rejected materials scrubbers for paint vapors; refining and/or terroving inks	Contain organic solids from dyes, resins, oils, solvents, etc.	Settling ponds for detention of paints, lime coagulation of printing inks
Acids	Dilute wash waters; many varied dilute acids	Low pH, low organic content	Upflow or straight neutraliza- tion, burning when some or- ganic matter is present
Detergents	Washing and purifying soaps and detergents	High in BOD and saponified soaps	Flotation and skimming, pre- cipitation with CaCl,
Cornstarch Evaporator condensate or bottoms when not reused or recovered, syrup from final washes, wastes from "bottling- up" process		High BOD and dissolved or- ganic matter; mainly starch and related material	Equalization, biological filtration, anaerobic digestion
Explosives Washing TNT and guncotton for purification, washing and pickling of cartridges		TNT, colored, acid, odorous, and contains organic acids and alcohol from powder and cot- ton, metals, acid, oils, and soap:	Flotation, chemical precipita- tion, biological treatment, aera- tion, chlorination of TNT, neutralization, adsorption
Pesticides	Washing and purification products such as 2,4-D and DDT	High organic matter, benzene- ring structure, toxic to bacteria and fish, acid	Dilution, storage, activated carbon adsorption, alkaline chlorination
phosphorus	Washing, screening, floating rock, condenser bleedoff from phosphate reduction plant	Clays, slimes and tall oils, low pH, high suspended solids, phosphorus, silica and fluoride	Lagooning, mechanical clarity cation, coagulation and settling of refined waste
	Residues from manufacturing synthetic resins and from dyeing synthetic fibers	Normally high BOD and HCHO, toxic to bacteria in high concentrations	Trickling filtration, adsorption on activated charcoal

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Industries producing wastes	Origin of major wastes	Major characteristics	Major treatment and disposal methods
Plastics and resins	Unit operations from polymer preparation and use; spills and equipment washdowns	Acids, caustic, dissolved organic matte, such as phenols, formaldehyde, etc.	Discharge to municipal sewer, reuse, controlled-discharge
Fertilizer	Chemical reactions of basic elements. Spills, cooling waters, washing of products, boiler blowdowns	Sulfuric, phosphorous, and nitric acids; mineral elements, P. S. N. K. AI, NH., NO., etc. Fl. some susp. solids	Neutralization, detain for reuse, sedimentation, air stripping of NH,, lime precipitation
Toxic chemicals	Leaks, accidental spills, and refining of chemicals	Various toxic dissolved elements and compounds such as Hg and PCBs	Retention and reuse, change in production
Mortuary	Body fluids, washwaters, spills	Blood salt, formaldehydes, high BOD, infectious diseases	Disch. to municipal sewer holding and chlorination
Hospital-Res Labs	Washing, stenlizing of facilities, used solutions, spills	Bacteria, various chemicals radioactive materials	Disch to mun sewers; holding and biol, aeration in large facilities
Steam power	Cooling water, boiler blow- down, coal dramage	Hot, high volume, high mor- ganic and dissolved solids	Cooling by actation, storage of ashes, neutralization of excess acid wastes
Scrubber power plant wastes	Scrubbing of gaseous combustion products by liquid water	Particulates, SO ₂ , impure absorbents or NH ₃ , NaOH, etc.	Solids removal usually by
Coal processing	Cleaning and classification of coal, leaching of sulfur strata with water	High suspended solids, mainly coal, low pH, high H,SO, and FeSO.	Settling, froth flotation, drain- age control, and sealing of mines
Nuclear power and i	radioactive materials Processing ores; laundering of contaminated clothes; research lab wastes; processing of fuel; power-plant cooling waters	Radioactive elements, can be very acid and "hot"	Concentration and containing, or dilution and dispersion
Non-point sources	Dirt, dust, combustion prod. runoff, salt runoff, organic matter runoff	Various but largely mineral and organic matter	Sealing sources, holding and treating by various means

Finally, the following charts illustrate some of the human health arguments in favor of CT. TABLE 4 $^{(4)}$ is a tentative Dutch list of specific industrial pollutants with public health concern.

	Arsenic	cancer?	
TABLE 4	Asbestos	cancer? mesothelioma	
	Benzo(a)pyrene	cancer?	
	Beryllium	herylliosis	
	Cadmium	cardiovascular disease?	
	Castor bean dust	sensitization	
	Chromium (chromates)	cancer?	
	Cotton dust	byssinosis?	
	Fluorides	plants, animals, sensiti-	
		zation?	
	fron ore (silica)	cancer?	
	Hydrogen chloride	irritation airways	
	Lead	CNS? ALAD reduction	
	Manganese	lung, CNS?	
	Nickel (Carbonyl)	cancer?	
	Organophosphorous epds	accidental release	
	Organochlorine epds	body burden, chlorine acne?	
	Platmom	platinosis?	

The table

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The next chart attempts to establish human carcinogenic agents and circumstances.

TABLE 5 (Carcinogenic Agents) (68)

ė

Agent or circumstance Occupa- tional Medical Social Allatoxin + Liver Allatoxin + Mouth, pharynx, larynx, cophagus, liver Allatoxin + Bladder Allexhain + Bladder Allexhain + Bladder Arsonici amines: + Bladder 4-Aminodiphenyl + Bladder 5-Naphthylamine + Bladder 2-Naphthylamine + Bladder 2-Naphthylamine + Ling, pleura, periioneum Benzine + Lung, opleura, periioneum Bisulphan + Marrow Cadmium ⁴ + Lung Choromith ⁴ + Lung Chorominth ⁴ + Lung Chorominth ⁴ + Nasal sinuses (hardwool) + Nasal sinuses Immunosuppressive drugs + Nasal sinuses Ionizing radiations ⁶ + Nasal sinuses Leainer goots manufacture + Nasal sinuses Leainer goots manufacture + Nasal sinuses Verantrikin (causing obesity) + Nasal sinuses, lung Polycycle hydrocarbons + +		Exposure			- Site of cancer	
Altaokin Alcoholic drinks Alcoholic drinks Al	Agent or circumstance	-	Medical	Social		
Alcoholic drinks + Mouth, pharyns, laryns, esophagus, liver Alkylating agents: Cyclophosphamide + Bladder Melphalan + Marrow Aromatic amines: 4-Aminodiphenyl + Bladder 3-Naphthylamine + Bladder 3-Naphthylamine + Bladder 4-Senice + Bladder Arsenic ⁶ + + + Charge - Comparison - Comp	Aflatoxin			+		
Cyclophospitamide+BladderMetphalan+MarrowAromatic amines:+Bladder+-Aminodiphenyl+Bladder2-Naphtylamine+Bladder2-Naphtylamine+BladderArsenic*++Arsenic*+HadrowArsenic*+Lung, pleura, peritoneumBenzene+LungBis(chloromethyl)ether+LungBis(chloromethyl)ether+HouthChowing (betel, tobacco, lime)+MarrowChromium*+BladderFurniture manufacture+Bladder(hardwood)+Nasal sinusesImmunosuppressive drugs+Reticuloendothelial systerIonizing radiations*++Nastal sinuses+Leariner goods manufacture+Vagina+Transplacental (DES)+Voernutition (causing obesity)+Phenacetin+Phenacetin+Skintusoma hematobium+Chloserdus manufacture+Unopposed+Tassplacental (DES)+Vagina+Reproductive history:+Lare age at 1st pregnancy+Zero or low parity+Skintusoma hematobium+Chloserdus unentit+Steroids+Anabolic (navmetholone)+Contraceptives+Contraceptives+Cho				+	•	
CyclophospiannieiMarrowAromatic amines:+Marrow4-minodiphenyl+Bladder2-Naphtylamine+Bladder2-Naphtylamine+Bladder2-Naphtylamine+BladderArsenied++Arsenied+LungBenzene+LungBis(chloromethyl)ether+LungBis(chloromethyl)ether+HarrowCadmiumd+HarrowChowing (betel, tobacco, lime)+LungChlornaphazine+BladderFurniture manufacture+Nasal sinusesfurniture manufacture+Nasal sinusesIonizing radiations"++Ionizing radiations"+Nasal sinusesLeainer goods manufacture+Nasal sinusesLeainer goods manufacture+Nasal sinusesUnopposed+YaginaOvernutrition (causing obesity)+*Phenacetin+Hometrium, gallbladdChloroschis menti+HoderChloroschis menti+CorayParasites:Contraceptives+LiverAnaboli (cavmetholone)+LiverAnabolis (avmetholone)+LiverAnabolis (avmetholone)+LiverAnabolis (avmetholone)+LiverAnabolis (avmetholone)+LiverAnabolis (avmetholone)+LiverAnabolis (avmet					Bladder	
Arematic amines: 4. Aminodiphenyl + Bladder 4-Aminodiphenyl + Bladder 2-Naphthylamine + Bladder Arsenie* + Harrow Benzene + Lung Bis(chloromethyl)ether + Lung Bis(chloromethyl)ether + Marrow Chomium* + Prostate Choromiphazine + Mouth Choromiphazine + Nasal sinuses Immunosuppressive drugs + Reticuloendothetial system Ionizing radiations* + Nasal sinuses Isoprop:* alcohol manufacture + Nasal sinuses Veziner goods manufacture + Nasal sinuses Vagina Yagina Yagina Overnutrition (causing obesity) + Tindometrium, gallbladd Phenacetin + Skin, scrotum, lung Reproductive history: <td></td> <td></td> <td></td> <td></td> <td></td>						
4-Aminodiphenyl + Bladder Benzidine + Bladder 2-Naphthylamine + Bladder Arsenic ⁴ + + Skin, lung Arsenic ⁴ + + Skin, lung Assestos + Lung, pleura, peritoneum Benzene + Harrow Bis(chloromethyl)ether + Lung Bisulphan + Prostate Chomium ⁴ + Renzow Chomium ⁴ + Lung Chomium ⁴ + Bladder Furniture manufacture + Mouth Immunosuppressive drugs + Reticuloendotheial syster Ionizing radiations ⁴ + Nasal sinuses 'Leather goods manufacture + Nasal sinuses 'Leather goods manufacture + Nasal sinuses, lung 'Leather goods manufacture + Nasal sinuses, lung 'Leather goods manufacture + Nasal sinuses, lung 'Leather goods + Skin, scrotum, lung Nickel ⁴ + Skin, scrotum, lung	-		+		MELIOW	
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UV light + + Skin, lip	Tobacco smoking			+	Mouth, pharynx, larynx, lung, esophagus, bladde	
	UV light	+		+		
VIBVECHOFIOC T LIVELANDIOSACOMAL	Vinyl chloride	+			Liver (angiosarcoma)	

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The next chart illustrates some of the industrial responses by use of ET to cope with the enormous problems. TABLE 6 is a classification of waste gas treatment equipment by separation forces. (50, p.50)

	Separation principle	Types of equipment	Examples of application
	discrimination	Mechanical filters, screens, grids	Coarse particulates, dust
	Gravity	Sedimentation chambers	Particles > 80 µm dia.
	Incrtial, centrifugal forces	Cyclones, impactors, pressure drop washers, N-washers	Particles > 2 µm dia.
	Electrostatic forces	Electrofilters	Dry dusts, mist, certain aerosols, H-SO ₄ mist
Weak bonds are formed, reversible	Adsorption on activated carbon	Adsorption towers	Solvent vapours, various compounds in malodorous waste gas streams
	Adsorption on special adsorbents	Adsorption towers	Recovery systems, e.g. SO ₂ on lime
	Solution or suspension in solvents, mainly in water	Different types of washers and gas scrub- bers, addition of condi- tioning agents	Soluble gases, wettable dusts, acrosols, mists, dusts following suitable conditioning
	Change in physical state (gas – liquid)	Coolers, condensers	Vapours of solvents of lower vapour pressure, mercury vapours
Chemical modifica- tions, reversible	Pollutant-specific chemical reactions	Washers	Acidic gases in an alkaline medium
Chemical modifica- tions, irreversible	Pollutant-specific chemical reactions in the adsorption liquid with the destruction of pollutant	Washers with addition of chemicals	Reactive gases, e.g. phosgene (with ammonia) mercaptans with oxidizing agents
Thermal modifica- tions	Product-specific reactions		Nitious oxides and ammonia to form nitroger gas
	Pyrolytic destruction of pollutant	Dedicated incinerators	Flares for excess hydro- carbon
	Catalytic systems	Incincration in normal furnaces for energy generation	Destruction of malodorou off-gases by leeding into boder firing

TABLE 6 (Classification of Waste Gas Treatment Equipment)

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Industrial Processes and Emissions

PART I

The eventual plan for this section is to list the major and various industrial production and manufacturing systems emitting chemicals and various wastes into the air, soil and water. This is as enormous an undertaking, as it is necessary. The following alphabetical list is only indicating the direction such work must take. It will have to be a composite work by many specialist.

Air

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II I II II

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<u>Water</u>

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	Agriculture Asbestos Bakery – Brewery – Cannery –	grease, sugar, flour, fruit, detergents, 3000-5000 ppm BOD beer slops, suspended solids, yeasts, organic nitrogen, 390 ppm BOD high BOD, treatment chemicals, high wash water, suspended solids (great variations, depending on product)
(see under 3692) sulfur oxide, nitrogen- oxide, fluorine (extremely complex and specialized), air pol- lution produced by acid	Cement Ceramic Coal	
gases, by hydrocarbons, et	c. Coffee -	pulp, fermentation wastes, turbidity, up to 15,000 ppm BOD
	Cornstarch Dairy -	various dilutions of milk, whey, alkaline wastes, various chemicals, lactic acid, 1000 ppm BOD
	Distillery Explosives Feedlot Fertilizer	a = a = 1 ide chemicals 33.000
	Fish -	water and solids, chemicals, 33,000 to 110,000 ppm පිCD
	Food processin Fuel and lube Fuel processin Glass Glue Hospital Iron foundry Laundry -	oil
	Machinery	

Water Air Meat packing - high nitrogen, high organic content, chemicals, organic nitrogen, ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, suspended solids Metal plating Metal plants Motor industry - suspended and dissolved solids, oil, Oil field wax sulfides, chlorides, mercaptans, phenols, cresylates, dissolved iron, etc. Oil refining - emulsified oil, waste caustic, caustic sludges, alkaline waters, acid sludges, acid waters, special chemicals, sulfuric acids, etc. Paint Paper (see 3411) Pesticides Petrochemicals Pharmaceutics- inorganic solids, various chemical wastes, vitamins, including B₁, B₂, B₁₂, streptomycin, lysin, sulfaquinazoline, nicarbazin, glycanides, up to 14,000 ppm BOD, etc. Photography Plastics Pulp (see 3411) Resin - nitrogen, phosphates, starch, solids Rice Rubber Slaughterhouse Steam Power Plant and CO₂, SO₂, SO₄, Steel mill - cyanogen compounds, phenols, ore, NO_x, etc., phenol and coke, limestone, acids, alkalis, oxygen-demanding matter, oils, wash waters, H₂SO₄, flue dust solids, iron FeSO₄, NH₃, etc. oxide, alumina, silica, carbon, lime, magnesium, ash, sulfur, CO₂, CO, CH_4 , N_2 , O_2 , C_2N_2 , CS_2 , H_2S , etc. Soap and detergents flume water, pulp-press water, Sugar lime-slurry, Steffen waste, chemicals, etc. Tannery (see 3237) Textiles (see 3211) Toxic chemicals Wax Winery Wood

For easier international listing and identification a process, once selected for extensive treatment, receives its I.S.I.C. numeric index number.

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For such treatment a content page offers a concise overview. The content page is subsequently elaborated on the pages following it.

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It would be the purpose of the proposed ring-note-book to update these informations on the content page and those more detailed pages following, from time to time. Every UNYDO project needs to be aware of the environmental parameters emerging from such a systematic and detailed presentation.

Index Number and Name of Industry				
0.	Introductory			
1.	Technological Processes:			

2. Environmental Impacts:

3. Emission Assessment:

4. Problems and Solutions:

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3211/TEXTILES

- 0. Introductory
- 0.1 Raw cotton is carded, spun, spooled and warped, slashed (filled with starch), drawn, and woven or knitted into cloth before being sent to the finishing mill
- 0.2 Wool from sheep, camels, alpaca, llama, and other fur/hair with large cell structure
- 0.3 Synthetic fibres are essentially composed of pure chemical compounds and have no natural impurities
- 0.4 Chemical modifications of cotton or wool, like AMC (acrylamido-methylated cotton), cotton cellulose bearing aromatic amino groups, cellulose carbamate, methylolated cellulose carbamate, methylolated carbomylethylated cellulose, etc.
- 1. Technological Processes:
- 1.1 Raw cotton conversion to cloth: desizing, scouring, bleaching, mercerizing, dyeing, printing, finishing
- 1.2 Raw worl: scouring, stock dyeing, carding, fulling, washing, carbonizing, piece dyeing, bleaching and brightening
- 2. Environmental Impacts:

The second second

- 2.1 Air: dust and fly liberation during opening of bales of cotton or wool and during carding of fibres. Organic compounds. Waste incineration, generation of steam and hot water (plants burning gas, oil cr coal). Volatile organic compound (VOC) emission from any textile process involving a heating stage. Oil emission. Emission of chemicals during dyeing, printing and finishing.
- 2.2 Water:starch wastes, causcic wastes, general wastes (from washing, bleaching, dyeing and finishing of cotton). Wool wastes originate from scouring, dyeing, oiling, fulling, cabonizing and washing processes.

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3.	Emission Assessment
3.1	Emission in textile operations is particularly noticeable in particulates and solvents. Reduction in organic emissions involve a critical review of processes: - reducing the ievel of organics in the fabrics entering the
	tenter or curving ovens
	 substituting certain reagents by less volatile ones to
	accomplish the same desired end product
	 reducing both the air flow and the operating temperatures of
	the equipment to accomplish the same desired end point.
3.2	Even the best housekeeping practices will reduce the BOD load only by 5% to 10%. Pollution loads especially heavy in cotton kierning, sizing and in the amount of chemicals used in other processes. Process chemicals are fatty-acid soap, Na ₂ CO ₃ (soda ash), Na ₆ P ₄ O ₁₃ (quadrafos), pine oil, proxol T, CH ₃ COOH (acetic acid 84%), H ₂ SO ₄ (sulfuric acid), chrome mordant, glauber salt, monochlorbenzene, detergents, etc.
4.	Problems and Solutions:
4.1	Problems particulates and volatile organic compounds
4.2	Solutions scrubbers, electrostatic precipitators, demisters, afterburners, CT substitution of steam ranges for oxidation of dyes in place of dichromate-acetic acid baths use of less caustic in kierning use of low-BOD dispersing, emulsifying, leveling etc agents etc replacement of soap in scouring replacement of Na ₂ CO with detergent Na ₂ SO ₄ mixture to reduce high alkilinity of waste etc.

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ad 1: The antiquity of textile manufacturing has caused proven conventional ways. The current astronomical need for ever new textiles has caused refinements of the conventional approach relying increasingly on machine and chemical processes. A natural product is far removed from ecological methodologies. With hundreds of thousands of local textile mills and shops, particularly in developing countries, the environmental impact of this development is evident. The following tables illustrate the sophistication of conventional processes.

<u>Table 7</u> (Pollution Loads Contributed by Various Processes) (33)

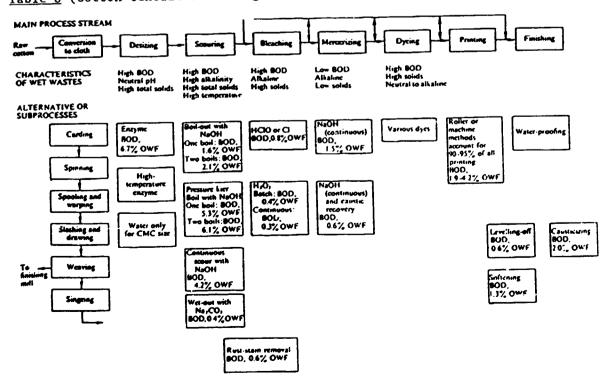
Department	Process	lb POD/1000 lb cloth*	% of total
Desizing		53	35
Scouring	pressure kier, first scour	53	16
J.J.J.	Either pressure kier, arst scoul	8	I
	Or continuous scour	42	15
	Average	47	
	Subtotal (scouring)		32
	Succore: (Souching)	0.5-32	15-30
Dyeing	Color choo waster	12	7
Printing	Color-shop wastes Wash after printing, with soap	17-30	17-30
	Wash after printing, with Wash after printing, with detergent Subtotal (printing)	7	7
Disservices	Hypochlorite bleach	8	3
Bleaching	Peroxide bleach	3	l i
Mercerizing		6	
Total		125-250	

Table 8 (Cotton-textile Finishing Process Flow Chart) (33)

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<u>Table 9</u> (Wool-textile Production Process Flow Chart) (35, p.313)

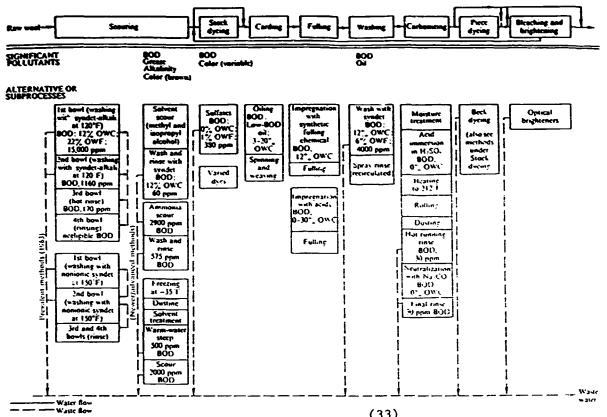


Table 10 (Analysis of Waste from Woolen Mill)(33)

	Alkalinity*			Solids			
Method	pН	CO; ppm	HCO, . ppm	Total, ppm	Fixed, ppm	Volatile, ppm	BOD, ppm
Grease scour, 1st bowl, soap-alkali	9.7	4870	7340	64,448	19,133	45,315	21,300
Grease scour, 1st bowl, detergent-Na,SO,	8.0	0	6442	60,593	19,889	40,012	15,400
Grease scour, 2nd bowl, soap-alkali	10.4	9155	2214	25,624	15,131	10,493	4,780
Grease scour, 2nd bowl, detergent-Na,SO,	8.3	16	463	6.368	2,086	4,478	1,160
Grease scour, 3rd bowl, soap-alkali	9.7	355	154	1,129	555	574	255
Grease scour, 3rd bowl, detergent-Na,SO,	7.3	0	75	1,609	525	1,083	170
Stock dyeing, acetic acid	7.3	18	803	3,855	2,248	1,266	2,182
Stock dyeing, ammonium sulfate	6.7	0	194	8,315	3,782	4,533	379
Wash after fulling, 1st soap, soap used for fulling	10.0	2117	584	19,267	4,771	14,489	11,455
Wash after fulling, 1st soap, detergent used							ł
for fulling	9.7	380	60	4,830	977	3.853	4,000
Neutralization following carbonizing, 1st running rinse	2.2	0	0	2.241	193	1,048	28
Neutralization following carbonizing, Ist soda-ash bath	8.5	517	2788	9,781	9,559	222	28
Optical wool bleaching in dye kettles	6.0	0	281	908	376	532	390

*No free hydroxide present in any waste samples.

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Confronted with modernization of mills and increase in waste and pollution, a pioneering number of mills have successfully begun to alter different steps in the processes.

The Research Triangle Park (NC), US EPA has successfully proven that the operating temperature of its curing/finishing tenters through changes in the resin/catalyst system, reduced not only the visible emission level, but also the non-condensible hydrocarbon levels.

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It is also possible to completely eliminate emission problems in screen printing installations by shifting from oil-based to water-based media. Solvents used in textile manufacturing should be recovered as effectively as possible. Scouring the fabric in a low boiling point organic solvent (usually a chlorinated hydrocarbon) to remove less volatile organic compounds is a method of reducing emissions of high boling-point compounds, i.e. visible emissions. (35)

Lanolin in woolen-mill wastes has often been recovered through solvent extraction. A cleaning-solution solvent, such as carbon tetrachloride or benzene, is generally used. The waste of wool grease in mills around the world goes into the hundreds of thousands of tons annually. Recovery with its inherent large BOD reduction is an important step in any waste-treatment plan.

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3231/TANNERY

0. Introductory

Tanning is the art of converting animal skins into leather. The dry matter of the skin is almost entirely protein, of which 85% is collagen. The skin also contains minor amounts of lipids, albumins, gloubulin, and carbohydrates. The preliminary processes prepare the hide protein so that all undesirable impurities are removed, leaving the collagen in a receptive condition to absorb the tannin or chromium used in tanning.

1. Technological Processes:

Curing involves dehydration of the hide by drying it with salt or air in order to stop proteolytic enzyme degradation. Flashing removes the areolar (fatty) tissues from the skin by mechanical means.

Washing and soaking remove dirt, salts, blood, manure and nonfibrous proteins and restores the moisture lost during preservation and storage. Unhairing is accomplished by the use of lime, with or without sodium sulfide. This makes the skin more amenable to the removal of trace protein impurities. Lime splitting separates the skin into two layers. One is the more valuable grain layer. The other, the lower of flesh side, is called the split.

Bating prepares the hide for tanning by reducing the pH, reducing the swelling, peptizing the fibres and removing the protein-degradation products. It is usually accomplished with ammonium salts and a mixture of commercially prepared enzymes (trypsin and chymotrypsin). The skin becomes silky, slippery, smoother and more porous, increases in width and diminishes its wrinkles.

Pickling generally precedes chrome tanning and involves treatment of the skin with salt and acid to prevent precipitation of the chromium salts on the skin fibers. Degreasing removes natural grease, thus preventing formation of

metallic soaps and allowing the skin to be more evenly penetrated by tanning liquors.

2. Environmental Impacts:

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An equalized tannery waste, including rinses, is high in total solids (6000 to 8000 ppm) of which about half is NaCl. It contains about 900 ppm BOD, 1600 ppm total hardness, 120 ppm sulfide, 1000 ppm protein, and 30-70 ppm chromium. One gallon of waste characterized by hard ess, sulfide, chromium and sludge content is produced for each pound of hide received by the tannery. About 71% or 400 pounds of chemicals for each 1000 lbs of hide received by the tannery is discharged to waste. Salt constitutes 57% of the chemicals in this waste.

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3. Emission Assessment:

Treatment of tannery wastes is usually limited to equalization and sedimentation. Many tanneries discharge without treatment directly into coastal waters or into municipal sewage-treatment plants. Untreated wastes damage clog pumps and pipelines.

4. Problems and Solutions:

Activated sludge processes are able to render tannery wastes entirely suitable for discharge into streams. Milk of lime can be added periodically to avoid an acid effluent from the equalizing tank and to maintain the alkilinity level of the wastes above the minimum required for good clarification. Use aerobic lagoon for odor control. Biological treatment of equalized combined beamhouse and tanhouse wastes.

Tannery wastes originate from the beamhouse and the tanyard. In the beamhouse, curing, fleshing, washing, soaking, dehairing, lime splitting, bating, pickling and degreasing operations are carried out. In the tanyard, the final leather is prepared by several processes. These include vegetable or chrome tanning, shaving and finishing. The finishing operation includes bleaching, stuffing and fat-liquoring, and coloring.

The discharge from a tannery averages 8,000 to 12,000 gallons of waste water per 1,000 pounds of wet, salted hide processed. The waste average 8000 ppm total solids, 1500 ppm volatile (organic) solids, 1000 ppm protein, 300 ppm NaCl, 1600 ppm total hardness, 1000 ppm sulfide, 40 ppm chromium, 60 ppm ammonium nitrogen and 100 ppm BOD It has a pH of between 11 and 12 and normally produces a 5 to 10 percent sludge concentration because of the lime and sodium sulfide contents. The generally accepted procedure for waste treatment is equalization, sedimentation, trickling filtration, or activated-sludge treatment. The latter two biological treatments generally reduce the BOD by 85% to 90% and the sulfide by 100%. ^(35, p.335)

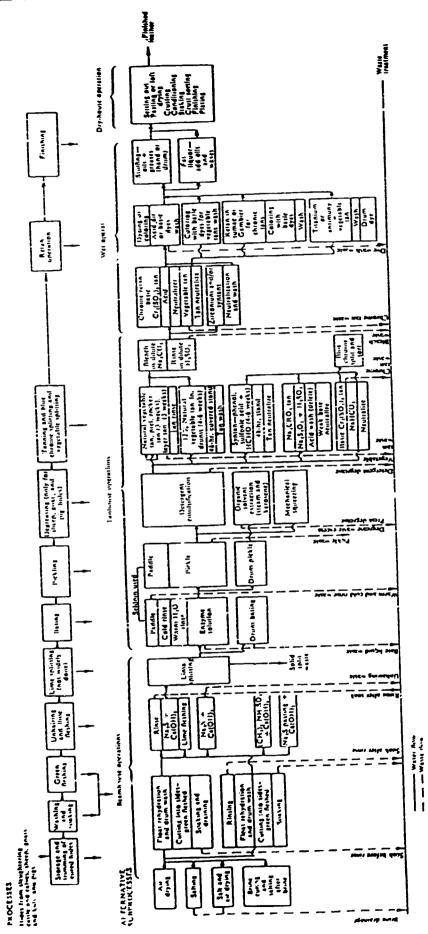
Wide fluctuations in the nature of tannery wastes due to intermittent dump discharges make these wastes difficult to manage. There are several hundred thousand tanneries in the world. Treatment of wastes is usually limited to primitive sedimentation and equalization. Some chemical coagulation and sludge digestion are being started. Equalization is necessary to minimize the wide fluctuations in the composition of the waste caused by intermittent dump discharges of strong liquors. Sedimentation is necessary because of the large volumes of sludge (5 to 10 percent) present in the waste. If secondary treatment is resorted to, trickling filters and activated sludge systems are used. Innovations and CT is only slowly coming to the tanning industry which thus remains a major water pollution source.

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3411/PULP AND PAPER INDUSTRY
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     Introductory
     Raw materials (main feedstock):
     soft and hard woods, mixed tropical woods
     pulp, recycled pulp wastes
     waste paper, waste textiles, non-wood fibres
     straw, rice straw, bagasse, etc.
1.
     Technological Processes:
Mainly 4 ways of producing pulp:
- the kraft or sulfate process
 the sulfite process
 the semi-chemical process
 the mechanical process
1.1 Mechanical
     does not produce air pollution, but process needs energy by means
     of combustion furnace
1.2 Chemical
     soda and kraft pulping with sulphate
     bleached hard- and soft-wood kraft pulping
     chlorine bleaching most common
     single/double stage hypochlorite
     part substitution of ClO<sub>2</sub> (chlorine dioxide)
     see manufacture of cellulose derivatives like viscose, cellulose
     nitrates, cellulose acetates for which some pulp is used.
2.
     Environmental Impacts:
                          volatile SO<sub>2</sub>, SO<sub>3</sub>, H<sub>3</sub>SO<sub>4</sub> and reduced
2.1 Air
                Gas
                          sulfur compounds nitrogen oxides, chlorine
                          compounds, etc.
                Solid
                          residual organic material, inorganic solid
                          salts, particulates
2.2 Soil
                          BOD (Biological Oxygen Demand), COD (Chemical
2.3 Water
                General
                          Oxygen Demand), TOC (Total Organic Compound),
                          pH, color, turbidity.
                Dissolved wood reaction products, spent cooking and
                          bleaching chemicals, auxiliar chemicals,
                           chlorinated phenols, ammonia, sulfite, toxic
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materials, etc.Solidstotal suspended solids, fibres, bark, wood
particles, solid inorganic compounds, coliforms
(total and fecal), heavy metals, toxic
materials, oil, grease, etc.

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3.	Emission Assessment: bleaching process produces effluent high in organic compounds effluents in general high with BOD, SS effluent discharge insufficiently treated underdeveloped chemical recovery system high silica in rice straw disrupts chemical recovery operations
4.	Problems and Solutions: lack of advanced ET and CT for pulping central facilities for chemical recovery
	- efficient chemical recovery systems
	 closed water systems efficient techniques for desilication
	cheaper, simpler oxygen and peroxide technology recycling

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ad 1: Mechanical defibration of wood causes process water pollution by dissolved wood components like cabohydrates, lignin and extractions and by non-dissolved fiber resulting from mechanical treatment. To improve defibration and to increase pulp quality steam and chemical treatments of wood chips are implemented in which more wood components are dissolved. Yields in mechanical pulping range from 90% to 95%. An additional effluent load is casued by peroxide bleaching of this pulp.

<u>Process</u>	BOD ₅ kg/t	COD kg/t	
stone ground wood (SGW)	5.5 - 14.5	15 - 32	
refiner mechanical pulp (RMP)	9 - 20	20 - 45	
thermo-mechanical pulp (TMP)	21 - 29.5	46 - 65	
peroxide bleaching	14 - 19		

About 70% of the pollution is located in the process water, whereas 30% remains in the pulp. Thus market mechanical pulp mills sell about 1/3 of their pollution load together with their pulp. But usually mechanical pulp is integrated in paper mills nowadays.

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Chemical pulping requires roughly the dissolution of 50% of the lignocellulose raw materials. Different sulfites (NaOH alone, or mixtures of NaOH, Na₂CO₃ and Na₂S) do this. The dissolved organic matter and the cooking chemicals must be separated from the pulp in washing stages. Its efficiency is greater than 97% today. The resulting black liquor can be evaporated and burnt for steam generacion and chemical recovery. Nevertheless, black liquor treatment results in air and water pollution. The lignin content of the resulting pulp is still 3-6% and the pulp continues to contain other impurities. Bleaching stages intend to remove this. Conventional bleaching is done with chlorine compounds. During full bleaching 5-8% of the pulp is dissolved. The resulting effluents contain inorganic and organic chlorine compounds. It can not be burnt. Some of the chlorinated lignin degradation products and resin acids show toxic, mutagenic and cancerogenic effects. Their biodegradability is very low. Low molecular chlorinated compounds are very detrimental to aquatic systems.

Though worldwide the kraft pulping process is the dominating one, Wet German Pulp Production is based solely on the sulfite process using magnesium and calcium as bases.

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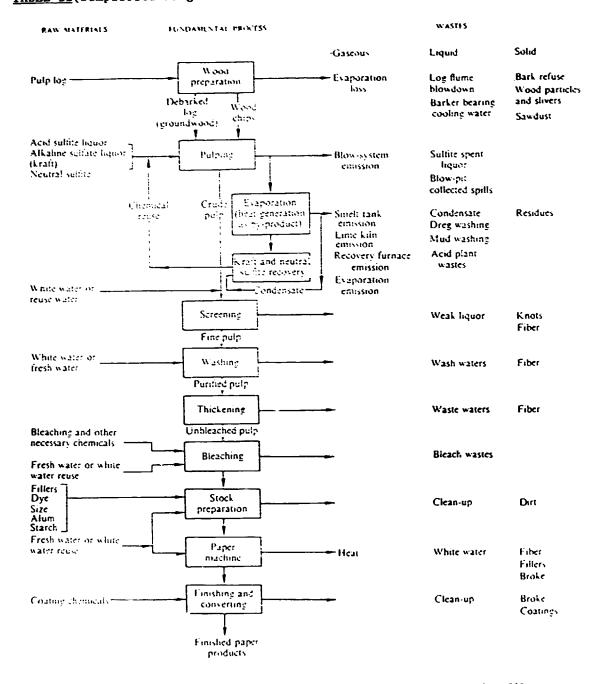


TABLE 12(Simplified Diagram of Fundamental Pulp and Paper Process)^(35, p.440)

Important in paper and board manufacture is therefore the fiber production process. Different pulp grades are used for various paper and board qualities. These differ in lignin contents. An intensified chemical tretment results in mechanical energy reduction for fiber separation. The so-called kraft process helps bring about such a lower lignin content.

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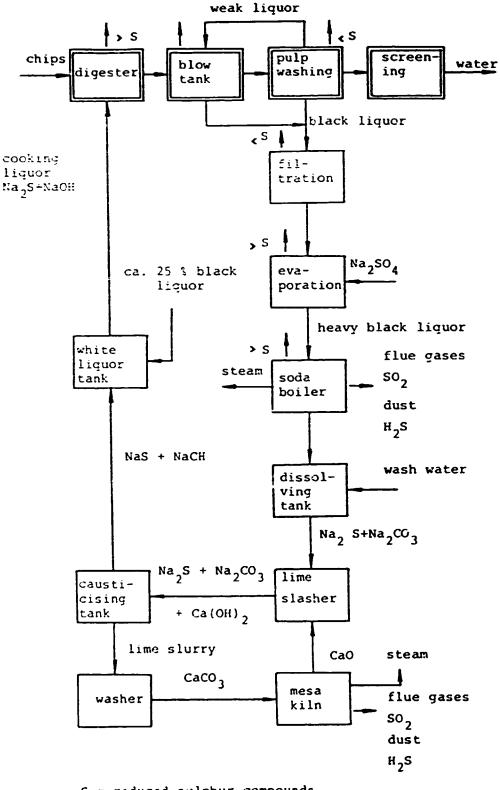
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TABLE 13 (Flow Chart of a Kraft Mill) (38)



S = reduced sulphur compounds (H_2S , CH_3 SH, $(CH_3)_2S$)

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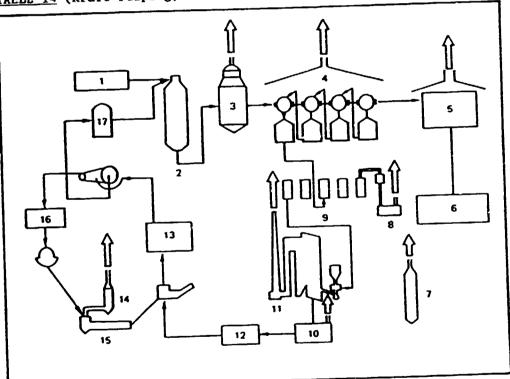
However, both the bonding potential of the fiber network and the dissolved organic matter in the black liquor are hereby increased.

The end-product paper requires during the normal course of its production remarkable amounts of water. Moreover, the chemical processes are severe water polluters, contaminating any water effluents coming in contact with them. The processes also cause air pollution by volatile sulfur compounds and in many cases chlorine compounds. The black liquor recovery processes add to the air pollution dust, NO_x, SO₂ and organic chlorine.

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While the kraft process remains popular, different approaches are being developed in response to environmental protection legislation.



TAPLE 14 (Kraft Pulping)⁽⁵⁰⁾

Fig. 11.9.1. Schematic diagram of the kraft pulp process with the main emission sources. 1, chip bin; 2, digester; 3, blowing tank; 4, washery; 5, bleaching plant; 6, pulp drying; 7, condensate stripper; 8, vacuum pump; 9, evaporator; 10, dissolving tank; 11, recovery furnace; 12, green liquor; 13, causticising; 14, flue gas scrubber; 15, lime kiln; 16, lime wash; 17 white liquor filter.

This sketch shows clearly, where these initial improvements could start successfully. In contrast to kraft or sulfate pulping, sulfite pulping developed, because it offers a wider range of different pulping options. Pulping can be carried out at different pH levels, ranging from strongly acid to strongly alkaline conditions, as well as at different temperatures in multi-stage processes.

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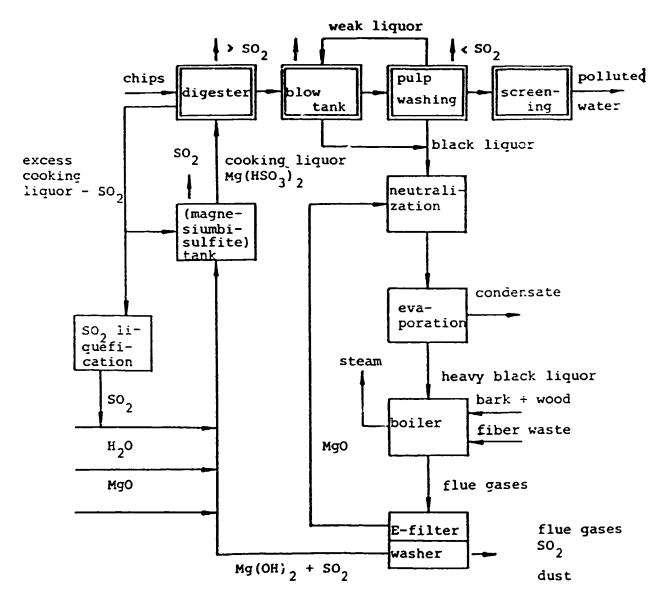
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For low pollution bleaching of pulp chlorine is substituted by chlorine dioxide, as well as by application of peroxide in prebleaching stages, oxygen or ozone bleaching.





The search for solutions to problems caused by processes is intensifying, as the following overview of select problems and practical solutions intends to illustrate.

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PROBLEMS

- kraft process
- air emissions with high H₂S etc levels
- effluent discharge to recovery water bodies with high BOD, COD, SS and toxic water pollution

SOLUTIONS

- substitute caustic anthraquinone pulping process

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- electronic precipitators and scrubbers to control air pollution
- extensive effluent treatment; primary and biological treatment; sludge sedimentation, sand filtration, decantation, separation; save-all filter to recover fibers in white water; use of waste-water as feedstock; 90% white water recycling to pulper; anaerobic treatment of waste liquor reduces BOD by 90% and produces significant amounts of marsh gas; clarifier treatment in stabilization pond/aerated lagoons and use of clarified effluent on land for crop irrigation
- de-inking process; CT with bleaching process various oxygen methodologies
- substitute Cl0₂, H₂O₂, etc. chlorinated phenols
- central facilities for chemical cooking chemicals recovery and new methods for alkali, lignin, etc., recovery, etc.
- . desilication technology and high silica removal of silica before the evaporation process

Increasingly various wastes are recovered or recycled as new process materials. The following examples illustrate this.

- heat: use of wood and fiber wastes instead of fuel oil or coal
- pulp washing: waste-paper based mills can readily recycle filtered waste water to wash pulp; fibers are returned and processed; water recycled to various stages
- anaerobic digestion: waste treatment produces considerable amounts of marsh gas
- sludge reuse: use primary sludge for other paper mill processes
- water recycling: partial closure of cycles in same mill ~
- screening and washing: white and black water recycling
- black liquor: conventional CRS; cooking chemicals recovery and organics burnt for heat production

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- cooking: sodium sulfide and sodium carbonate effluent evaporated; organics used as fuel for heat production
- sulfite cooking: waste liquor used for alcohol fermentation and yeast production
- clarification: solids used as fuel
- activated sludge: treatment w recycled
- bleaching: extraction; separate lignin used as adhesive agent or raw material for dyestuffs.

The following tables show the difficulties to be encountered as well as some of the successes in altering conventional pulping processes.

TADIE 16	() ; =	Pollution	Emicsions	from	Various	Pointe	٥f	Kraft	Process) ⁽⁵⁰	, p.513)
INDLE 10	(AII	FOLIGITON	Emissions	1100	various	romes	01	VIGIC	riocess)	

	Emission					
Sourc e	Reduced sulfur compounds	Sulfur dioxide (SO2)	Chlorine dioxide	Nitrogen oxides (NO _x)	Particulat/ matter	
Digestry	x					
Washery	x					
Bleaching plant			x			
Evaporators	х					
Recovery furnace	x	X		х	х	
Smelt dissolving tank	x				x	
Lime kiln	х	x		х	х	
Tall oil recovery	х					

<u>TABLE 17</u> (Typical Emissions after Reduction Changes in Kraft Process)⁽¹³⁾

c	Emission rate (kg S/t of pulp)					
Source	H ₂ S	CH3SH	CH3-S-CH3 CH3S-SCH			
Digester (batch)	0 - 0.1	5 0 -1.3	0.05-3.3	0.05-2.0		
Digester (continuous)	0 - 0.1	0.5 -1.0	0.05-0.5	0.05-0 4		
Washery	0 - 0.1	0.05-1.0	0.1 -1.0	0.1 -0.8		
Evaporator (indirect)	0.05- 1.5	0.05-0.8	0.05-1.0	0.05-1.0		
Recovery furnace (after direct contact evaporator)	0 -25	0 -2	0 -1	0 -03		
Recovery furnace (without			·			
direct contact evaporator)	0 - 1	0 –0.01	0 -0 01	0 -0.01		
Smelt dissolving tank	0 ~ 1	0 -0.08	0 -0.5	0 -0.3		
Lime kiln	0 - 0.5	5 0 -0.I	0 -0.1	001		
Settling basin	0 - 0.0)5 0 -0.02	0 -0.01	0 -0 62		

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TABLE 18 (Characteristics of Kraft Mill Wastes)⁽³⁵, p.442)

Characteristic	Maximum	Minimum	Average
pH Total alkalinity, ppm Phenolphthalein alkalinity, ppm Total solids, ppm Volatile solids, % Total suspended solids, ppm Volatile solids, % BOD, 5-day, ppm Color, ppm	9.5 300 50 2000 75 300 90 350 500	7.6 100 0 500 60 75 80 100	8.2 175 0 1200 65 150 85 175 250

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3692/CEMENT

0. Introductory

Cement is a finely gound hydraulic binder for mortar and concrete. It consists essentially of compounds of calcium oxide with silicon dioxide, aluminum oxide and iron oxide produced by sintering and smelting.

When mixed with water, cement hardens both in air and under water and remains hard under water.

1. Technological Processes:

Material components are won and crushed in the quarry. Thereafter they are ground to raw meal in a certain mixing proportion. At the same time the material is dried with kiln exhaust gas in the mill. The finely ground raw meal is put into intermediate silos where it is homogenized.

The exit gas is dedusted in electrostatic precipitators. For klinker burning, the raw material is first heated with the exit gas of the rotary kiln in the suspension preheater. It generally consists of four cyclone stages. The rotary kiln exit gas passes through the preheater in counterflow from below to the raw meal and for that reason there is an intensive heat exchange between gas and the raw meal in the upper cyclone stages. In the connecting duct between the lowest cyclone and the rotary kiln, the calcining is started at a temperature of about 820 degrees C - 870 degrees C and the carbon dioxide escapes from the calcium carbonate.

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2. Environmental Impacts:

Emissions of dust and gaseous pollutants Noise and vibrations due to machines and quarry explosions. Exhaust gases are mainly composed of nitrogen (N_2) , carbon dioxide (CO_2) , oxygen (O_2) and water. Exhaust gases can also contain small quantities of sulphur dioxide (SO_2) , nitrogen oxide (NO_x) , carbon monoxide (CO) and organic carbon compounds.

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3692	2/
3.	Emission Assessment
3.1	Dust emission being quite irregular must be continuously monitored. Working measurement devices for nitrogen monoxide, sulphur dioxide and carbon monoxide ought to be installed in the clean gas stacks of the rotary kilns.
	All emissions can be reduced, because of add-on pollution control devices and management measures.
4.	Problems and Solutions:
	Cement factories are a good example for the application of ET and CT.

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Chemicals and Risks

PART II

The European Inventory of Existing Commercial Chemical Substances (EINECS) lists 100,185 materials. To understand them and their influence upon the environment is the stupenduous common task of science, industry and governmental organizations on the local, national and international level.

The Chemical Abstract Services (CAS) of the American Chemical Society registered in 1986 the seventh million chemical formula. In 1970 this registry contained "only" 2 million entries. Of all these approximately 60,000 could be considered as important.⁽²⁴⁾

In Part II a start is being made to gather and characterize those chemicals which impact decisively and measurably upon the environment. A second selection criteria is their relationship to industrial processes.

The content page has the following format.

Chemical formula

Name of Chemical Substance

- 5. Sources:
- 6. Environmental Impact Assessment:
- 7. Problems and Risks:

Two recent studies (24, p.42-43) have attempted to list and study a concrete list of chemicals impacting on the environment. Among the 165 chemicals traced, are mainly hazardous ones. However, these will soon have to be included in forthcoming issues of the Digest. A selection follows.

 $C_{6}H_{7}N$; AlAsO₄ and many arsen combinations $C_{8}H_{14}N_{5}Cl$; $Mg_{3}Si_{2}O_{5}(OH)_{4}$ and all forms of asbestos $C_{6}H_{6}$; HCN and cyanide compounds Pb and various lead compounds Cd and Cadmium compounds C2H3C1302 C₆H₅CJ and Chlor compounds ; phenols C7H80 ; C₄H₈O₂ and carbon dioxan compounds CH₂O (formaldehyde) halogenmethane and CH₃Cl compounds PVC (PCB) C₂₀H₁₂ ; fluorine compounds C5H5N CS₂ ;

Before making a decision for this draft of a Digest a number of pollutants are examined as to their major sources and their principal effects. This will illustrate that such an overview is long overdue and very much needed by any and all involved in industrial development. The development officer faces an enormous responsibility and needs reference tables for industrial promotion and consultation.

	<u> </u>	·····
POLLUTANTS	MAJOR SOURCES	PRINCIPAL EFFECTS
Sulfur Dioxide	fuel combustion (coal, oil, cellulose, material) industrial processes	sensory and respiratory irritation, plant damage corrosion, adverse effect on health
Oxydants	atmospheric photochemical reactions involving nitro- gen oxides, organic gases, vapors, solar radiation	sensory and respiratory irritation, plant damage, provides indirectly an index of visibility re- duction due to photoche- mical aerosols, adverse effects on health
Carbon Monoxide	fossil fuel powered vehicles, fuel combustion, industrial process	reduction in the oxygen carrying capacity of blood
Total Gaseous Hydrocarbons	fuel combustion industrial processes, evaporation of hydrocarbons	visibility reduction, plant damage, sensory irritation, photochemical reactions involving reac- tive hydrocarbons; ethy- lene itself causes plant damage

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POLLUTANTS	MAJOR SOURCES	PRINCIPAL EFFECTS
Nitrogen Oxides (Nitric Oxide & Nitrogenic Dioxide	fuel combustion, industrial processes	visibility reduction, plant damage, sensory irritation are produced in photochemical reactions involving nitrogen oxides, nitrogen dioxide causes decresed visibility, adverse health effects
Total Aliphatic Aldehydes, Formal- dehydes and Algolein	fuel combustion, incine- tion of wastes, atmosphe- ric photochemical reactions	sensory irritations, plant damage, visibility reduction and adverse effects on health
Carbon Dioxide	combustion processes	used as an index of pol- lution from combustion operations
Suspended Particulate Matter	combustion, industrial and natural processes	visibility reduction, soiling
Hydrogen Sulfide	coke, distillations of tar, petroleum and natural gas refining, manufacture of viscose rayon, certain chemical processes	odor nuisance, caused death, toxic when large quantity escaped from a natural gas refining plant
Hydrogen Fluoride	heating of high tempera- ture of ovens, clays or fluxes containing fluorine; generally from steel mills, ceramic works, aluminum reduction plants and super- phosphate factories	damage to citrus and certain other agricultu- ral plants, flowers; affects teeth and bones of cattle when forage crop has been consumed
Lead	internal combustion engines, industrial emissions, open burning of lead paint coated wood	lead poisoning

A recent report (65) of the Global Environment Monitoring System of the UNEP-WHO listed air pollutants in fifty monitored cities. It is evident that cities in developing countries display the biggest environmental burdens.

Particulate Matter:

(Annual average number of days in which suspended particulate matter levels exceeded 230 micrograms per cubic meter)

New Delhi, India	294 days
Xian, China	273
Beijing, China	272
Calcutta, India	268
Shenyang, China	219
Teheran, Iran	174
Jakarta, Indonesia	173
Shanghai, China	133
Guangzhou, China	123
Bombay, India	100

Sulfur Dioxide:

(Annual average number of days in which sulfur dioxide levels exceeded 150 micorgrams per cubic meter)

Shenyang, China	146 days
Teheran, Iran	104
Seoul, South Korea	87
Xian, China	71
Beijing, China	68
Gourdon, France	46
Madrid, Spain	35
Guangzhou, China	30
Zagreb, Yugoslavia	30
Milan, Italy	29

Carbon Monoxide:

(These cities exceeded WHO guidelines for eight-hour concentrations over a five-year period---1980 to 1984)

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Paris, France	rank 1
Brisbane, Australia	2
Sao Paulo, Brazil	3
Los Angeles, USA	4
Melbourne, Australia	5
New York, USA	6
Chicago, USA	7
Toronto, Canada	8

C0/	CARBON MONOXIDE
5.	Sources: Incomplete combustion processes from gasoline and diesel motors; automobiles, trucks, buses, planes, motor boats Pumps and installations Industrial processes, heating facilities and incinerators Natural biological and non-biological sources Tobacco smoke
6.	Environmental Impact Assessment: Total CO emission into the atmosphere exceeds that of all other as pollutants combined CO is a potential industrial and a general environmental hazard.
7.	Problems and Risks: Absorbed into the lungs it combines with hemoglobin (Hb) in the blood to form carboxyhemoglobin (COHb)

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- ad 5: CO is one of the widest distributed and the most common air pollutant. It is colorless, odorless, tasteless gas, slightly lighter than air. It stems from incomplete combustion of carbon-containing materials. It is also produced by some industrial and biological processes. The latter's influence is, however, negligible. Estimates of man-made CO emissions vary from 360 to 600 x 10^6 tons/year. CO concentrations in urban areas depend on weather and traffic density. Relatively high pollution by CO is found in tunnels, garages, some workplaces and some homes with faulty cooking and heating appliances. Tobacco smoking is a very important source of exposure to CO.
- ad 7: CO inhaled combines reversibly in the lungs with Hb in the blood to form COHb. Its principal toxic properties are based on a competition with oxygen and a resulting tissue hypoxia. CO has an affinity for Hb about 240 times greater than that of 0. About 20% of the absorbed CO passes from the intravascular to the extravascular space and can react with myoglobin (Mb) to which its affinity is about 40 times greater than that of 0. CO is eliminated from the organism via the lungs. People living in polluted cities have been shown to have higher median values of COHb than people living in rural areas. Smokers have by far higher values than non-smokers. The inhalation of high CO concentrations leads to acute CO poisoning with many physiological and pathological changes. The manifestations consist of violent headaches and dizziness, followed by nausea, flickering vision and buzzing in the ears. In a further stage of CO intoxication mental changes appear. The capacity for judgement and decision-making is lost, sometimes with a state of mania excitation. In a final phase of acute poisoning tetanic muscle spasms may occur, followed by a comatose state accompanied by vomitting, diarrhea, drops in blood pressure and respiratory paralysis. As late effects of acute CO intoxication one may see encephalomalacias. Parkinsonism, Meniere-syndrom, hyperthyroidism and psychoses. In a healthy person a reduction in myocardial oxygen tension produces an increase in coronary blood flow. Even in healthy persons the ability to exercise maximally is impaired by exposure to CO. Questions related to fetal development must be of special concern.

	NITROGEN OXIDES AND OXYDANTS
5.	Sources:
	Nitrogen oxides are generated at high temperatures from nitrogen and oxygen in the air. The reaction can take place in a thunderstorm and in a gasoline or diesel engine, as well as in the flue gases from heating and from power plants and incinerators. Primarily nitrogen monoxide is created. Subsequently it slowly oxidizes to nitrogen dioxide. NO ₂ may, together with air, oxygen
	and solar UV radiation, initiate the series of reactions that ultimately lead to photochemical smog. By these reactions NO_2 may contribute to the formation of nitric acid, nitrates (i.e. PAN), and possibly also nitrosamines. Other stationary sources emitting NO_2 are plants manufacturing products such as nitric acid, explosives, fertilizers and
	petrochemicals. Tobacco smoking will contaminate the air with NO ₂ .
6.	Environmental Impact Assessment:
	Among the nitrogen oxides, NO_2 is the main compound of health importance. NO_2 has a reddish-brown color and a pungent odor. It is a strong oxidizing agent and biologically highly reactive. In air pollution it is one of the causes of photochemical smog.
7.	Problems and Risks:
	NO ₂ is a health hazard

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- ad 5: "Oxydants" usually refer to a number of compounds with oxidizing properties. They are often the result of complex chemical reactions in the atmosphere under the influence of solar radiation. Typical are NO₂, ozone and peroxyacetylnitrate (PAN). All this contributes to air pollution.
- ad 6: Globally and by itself NO₂ is not yet an important air pollutant. Locally it can be a health hazard. In urban areas it has considerable spatial and temporal variations. The rural background concentration is usually about 0.5 to 10 ug/m³. Annual means are typically of the order of 20-90 ug/m³, but hourly maximum values have reached 240-850 ug/m³ at street level in large cities. The indoor levels are usually somewhat lower than those outdoors, but gas-fired appliances may cause NO₂ concentration of several thousand ug/m³. Large amount of nitrogen oxides are inhaled during tobacco smoking; the intake calcualted to be 160-500 ug/m³/cigarette.⁽²²⁾
- Some NO, is dissolved in the mucus of the upper respiratory ad 7: tract. Subsequently it is fairly evenly distributed throughout the respiratory tract and is further spread in the body by the circulatory system. NO, absorption occurs in the lungs in the form of nitric or nitrous acid or their salts. The effects of NO, on humans is presently usually low. The same goes for other oxidants, specially Ozone. It is local in character. However, the sites are numerous. NO, and other oxidants interact with other environmental factors that can cause a synergistic effect, i.e. with sulfur dioxide or bacterial infections. NO, and many oxydants are sensory as well as pulmonary irritants. As sensory irritants they stimulate the few nerve endings in the throat or the eyes. This produces a burning and itching sensation. Tears can flow. Reflex mechanisms in the smooth muscles of the deeper airways are contracted, causing bronchoconstriction. NO, causes a number of systematic biochemical changes, for example, shown by the increased oxygen consumption need in the spleen and kidney, the increased lactole dehydrogenase (cytochrome) activity in the liver, kidney, spleen and serum, and, in some cases by polycythemia.⁽⁶²⁾ The most evident effects of NO₂ exposure are the changes in pulmonary function, as well as the synergistic effects of NO_2 and the development of respiratory infections.⁽⁵⁹⁾

ALTER ALTER

5.	Sources:
	Combustion of fossil fuels which contain sulfur compounds
б.	Environmental Impact Assessment:
	Sulfate formation has now become global Acid rain is a major concomitant of the spread of SO ₂
 7.	Problems and Risks:
	Sulfur dioxide is an irritant of the respiratory tract

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sulfates. Also possible is the secondary formation of sulfates under the influence of oxydants and UV light or due to the presence of catalytic metals. SO₂ in air pollution is never the sole agent operating. Often it combines with suspended particles, hydrocarbons, nitrogen oxides, trace metals, etc.

- ad 7: Sulfur dioxide is a moderately irritant gas that is strongly hydrophilic and thus very soluble in the mucosa of the respiratory tract. Thus SO₂ can affect lung functions; probably due to action on chemo-receptors in the upper airways and neutrally transmitted bronchoconstriction of small airways. SO₂ reach of the deeper airways can be fatal. Increase in incidence of respiratory disorders among children is marked. SO₂ can also affect reflex functions of the central nervous system.
- <u>TABLE 19</u> (Sulfuric Acid's Irritative Capacity for Animals in Descending Order)⁽⁵⁸⁾

Sulfuric acid Zinc ammonium sulfate Iron(III) sulfate Ammonium sulfate

ad 5:

Non-reactive Iron(II) sulfate Manganese(II) sulfate

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 H_2SO_4 $2nSO_4(NH_4)_2SO_4$ $Fe_2(SO_4)_3$ $(NH_4)_2SO_4$

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FeSO₄ MnSO₄

* Presented for equivalent amounts of sulfur and at comparable particle size, i.e. sub-micron; short-term exposures.

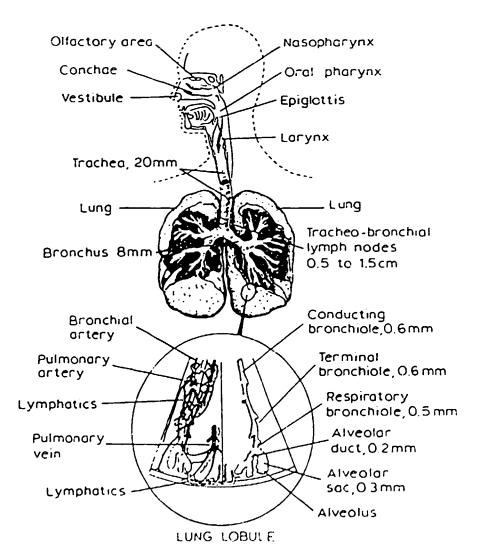
There was a substantial increase in bronchitis and in daily mortality during London's heavy sulfur dioxide smog winter of 1958-59.⁽³²⁾

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	Threshold levels(mg/m ³)			
	H ₂ SO ₄	SO ₂	$H_2SC_4 + SO_2$	
Effects				
Perception of odour and				
irritation of mucosa	0.6-0.85	1.6-2.8	0.3 + 0.5	
Suppression of dark				
adaptation	0.63-0.73	0.92	0.3 + 0.5	
Elevation of optical				
chronaxy	0.73	1.5	0.6 + 1.2	
Disruption of alpha rhythm	0.63	0.9	0.3 + 0.5	
Conditioning of	0.4	0.6	0.15 + 0.5 or	
electrocortical reflex			0.3 + 0.25	

TABLE 20	(Threshold Levels of SO ₂	required for	Effects	on Sensory	and
	Reflex Functions) ⁽⁷⁾				

TABLE 21 (Respiratory Tract)⁽³⁴⁾



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The fate of inhaled particles is dependent on their size and solubility. Normally ciliary action removes particles larger than 10-15 μ m. Non-hygroscopic aerosols remain airborn as particle size decreases and are exhaled. Total respiratory tract deposition in normal subjects reaches a minimum of about 10-20% for particles between 0.2 and 1.0 μ m, and increase for particles \leq 0.2 μ m. A major factor determining the probability of deposition of the smaller particles is their transfer from tidal to reserve air.⁽³⁴⁾

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Environmental Technologies and

Clean Technology

PART III

In the 1970's the concern with soft, appropriate and intermediate (middle) technologies received its first international support, when UNEP started the Pollution Abatement and Control Technology (PACT) data base. Information on practical technology actually being used in industry, the BPT (Best Practicable Technology) currently available began to be collected and prepared in suitable standard forms. It was to be particularly suited for developing countries' need for information on how to deal with their industrial pollution problems. PACT data were to be fed into the global INFOTERRA network; INFOTERRA being the international system by which UNEP refers those asking for environmental information to those who have agreed to provide such information.

Appendix A presents additional up-to-date information. Important at this moment is to know of the growing awareness of environmentally sound technologies as the most serious step in the last decade of the 20th century to try to manage environmental deterioration around the globe.

In Sweden SIIESTA (International Institute for the Assessment of Environmentally Sound Technologies) was established in 1988.⁽⁶³⁾

In Vienna UNIDC and the International Association for Clean Technology (IACT) organized an International Conference on Industrial Risk Management and Clean Technologies, 13-17 November 1988. IACT's introductory folder describes the purpose:

"Environmental policy has traditionally been directed at the control of waste after generation. Successive environmental legislation in industrialized countries is a testimony to the efforts to clean water, to reduce air pollution and to control waste disposal on land. These efforts have been proven only as imperfect solutions to the complicated problem of waste management claiming ever increasing funds from public and private sources. An interesting paradox has been witnessed: controlling pollution after its generation results in further waste products which require additional environmental and financial resources for their controlled final disposal. This viscious cycle of rising consumption of environmental resources and rising costs can only be avoided if cleaner technologies can be developed and applied. Cleaner technologies introduce a preventive approach to pollution. Based on this realization, cleaner technologies are the most effective way to prevent deterioration of environmental resources". (64)

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 International trade meetings in environmental technologies and concerns also began to focus on CT. Two examples suffice to bear this out:

The International Society for Environmental Protection (IGU), Vienna, Austria organized from 20-22 February 1989 the ENVIROTECH VIENNA 1989. The theme concerned "Chemistry - Technologies - Hazardous Waste" and an entire section of scientific papers and posters were dedicated to CT.

The prestigious and largest European fair of its kind, the ENVITEC 1989 met in Düsseldorf 10-14 April 1989 under the theme "Technology for Environmental Protection", holding numerous sessions and exhibits on CT.

It is hoped that this PART III of the Digest will become its most important section in the next years. While it will not neglect remedial ET, it will strive to present the latest breakthroughs and contributions of preventive CT.

The content page has therefore only two items.

Name of Industry

8. Remedial ET:

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9. Preventive CT:

Pollution abatement is either "destructive" (elimination, remedial ET, end-pipe, waste management, disposal sites) or "constructive" (process modification, byproduct recovery, resource recovery, recycling, preventive CT). The major tools remain physical/mechnical, chemical and biological. The last is gaining ground the fastest. UNIDO issues free of charge two monitors brimful of information from around the globe.

"Advances in Materials Technology: MONITOR" is compiled by the Development and Transfer of Technology Division, Department for Industrial Promotion, Consultation and Technology.⁽⁶⁶⁾ "Genetic Engineering and Biotechnology Monitor" is also compiled in the same UNIDO department. Each issue contains a section on Energy and Environment. Innovations in CT, applications and reports, are extremely encouraging for energy saving, minimizing environmental damages, minimizing risks, optimizing safety and pollution prevention. The Digest complements these Monitors and helps in the development of guidelines for the transfer of environmentally sound technologies for a sustainable development.

CEMENT 8. Remedial Environmental Technology: Most important concern is dust emission and proper dust control equipment. Electrostatic precipitators are expensive to install and prone to irreparable breakdowns in developing countries. As alternative cooling tower for gases and increase of their moisture content is proposed. Some of the highly alkaline precipitated dust is sold as agricultural lime. 9. Preventive Clean Technology: Three essentially different ways of nitrogen oxide formation in combustion systems. Investigations of the Research Institute of the Cement Industry in the FRG.

ad 9: Description of a CT:

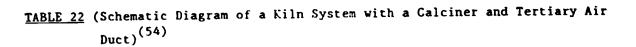
- The thermal NO formation from oxygen and molecular nitrogen of the combustion air at temperatures above 1600 degrees C in the combustion gas flow in and behind the actual flame.
- 2) The prompt NO formation from atmospheric nitrogen and oxygen in the so-called flame front which is normally characterized by the presence of substantial quantities of hydrocarbon radicals.
- 3) The NO formation in the flame from chemically bound nitrogen in the fuel.

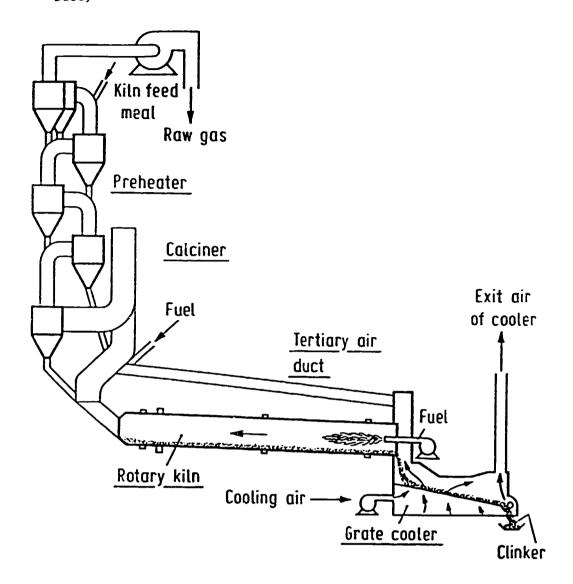
From the investigations of the Research Institute one can observe that in the rotary kiln of the cement plant at gas temperatures of over 1800 degrees C the thermal NO formation predominates. It depends on the temperature of the flame, on excess air, on retention time of the gases in the flame and on the form of the flame. In the secondary firing the fuel nitrogen is especially involved in NC formation, because of the low gas temperature. The main parameters are excess air and nitrogen content of the fuel.

It has furthermore been shown that the NO formation is superimposed upon a NO decomposition attributable to homogeous and to heterogenous reactions. For example, local under-stoichiometric combustion conditions in the secondary firing cause an evident NO decomposition. These mechanisms of decomposition can be optimized with regard to a low NO_x emission, without such measures having negative consequences on the rotary kiln operation, or on other relevant environmental parameters. There is also the possibility to avoid a higher NO formation already at the place of generation by optimizing the primary firing.

In terms of process technology the kiln plant can be subdivided into four main aggregates: preheater, calciner, rotary kiln and cooler. In the next illustration the calciner is the elongated connecting duct between the rotary kiln and the lowest cyclone.

- 53 -



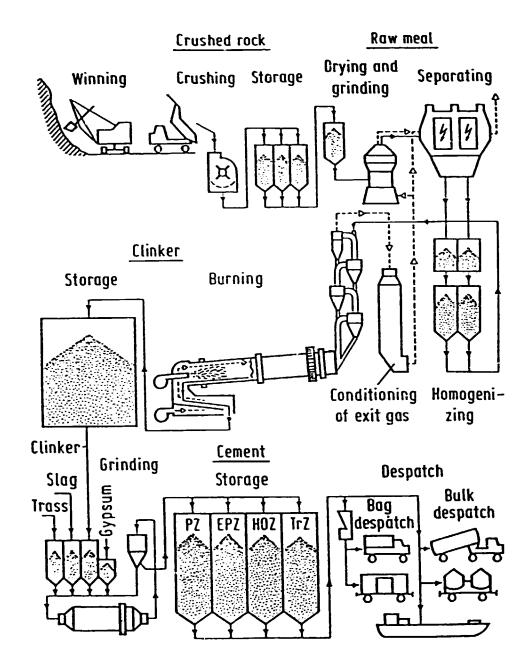


Fugitive dust can be removed by a less expensive system than eletrostatic dust precipitators. A fan can be installed to draw the dustladen air from different sources into a chamber where the cement is collected and recycled.

The emission of carbon monoxide and of organic carbon compounds can be reduced by technical firing measures. To reduce the emission of nitrogen oxide, technical firing as well as technical process measures can be applied.

In contrast, the reduction of NO $_X$ emission in ordinary kiln plants remains problematic. The quality of the cement clinker presupposes combustion conditions which normally lead to maximum NO formation.

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Contact: A. Scheuer Research Center of the Cement Industry Tannenstrasse 2-4 Postfach 30 10 63 D-4000 Düsseldorf 30 FRG

PULP	& PAPER
	Remedial Environmental Technology: The most important steps to decrease water pollution in paper mill are cooking down to low residual lignin contents of the pulp, high efficiency in pulp washing, chlorine free bleaching and evaporatio and burning of beachplant effluents together with cooking black liquor
	Preventive Clean Technology: Organosolv pulping process G&P closed water cycle for waste paper processing Oxygen bleaching Ozone bleaching Desilication of black liquor

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Ad 8 Two tables illustrate once more the enormous problems and challenges to both ET and CT.

Product	Waste, gal
Paper mills	
Groundwood	5,000
Soda	85,000
Sulfate (kraft)	64,000
Sulfite	60,000
Miscellaneous paper	
No bleaching	39,000
With bleaching	47,000
Paperboard	14,000
Strawboard	26,000
Deinking used paper	83,000

TABLE 24 (Average Waste Discharge per ton of Paper Product)

TABLE 25 (Typical Analysis of Wood Preparation Waste)⁽⁵⁵⁾

Characteristic	ppm
Total solids	1160
Suspended solids	600
Ash (suspended solids)	60 i
Dissolved solids	560
Ash (dissolved solids)	240
BOD, 5-day	250

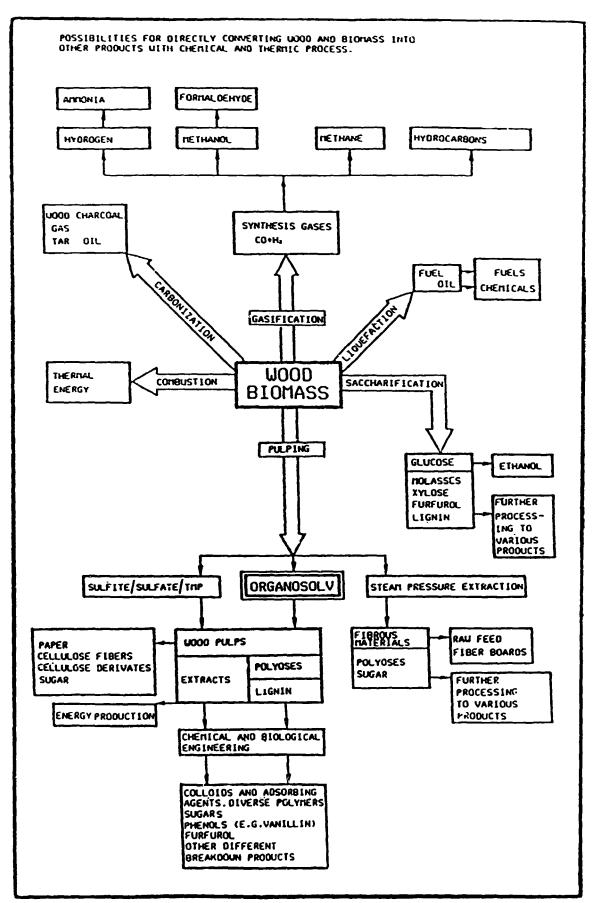
 Organosolv pulping is a new approach to pulp production. Mixtures of alcohol and conventional cooking chemicals show promising results. Aerobic biological treatment reduces COD of the condensates by 80-95%. Biological treatment of bleaching effluents becomes possible. Aerobic as well as anaerobic treatments yield COD reductions of about 50%. Application of alkali/0₂, alkali/H₂0₂, ozone or NO₂ in single stages and in combination reduces COD measured on conventional bleaching methods by 40-90%. Effluent from a nearby effluent free pulp mill will be possible by application of extended cooks yielding low residual lignin content, cnlorine free bleaching and biological waste water treatment.⁽⁶⁾ Table 26 shows the organosolv process.

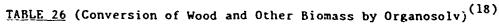
> MD ORGANOCELL Gesellschaft für Zellstoff- und Umwelttechnik mbH Planeggerstrasse 38 D-8000 München 60

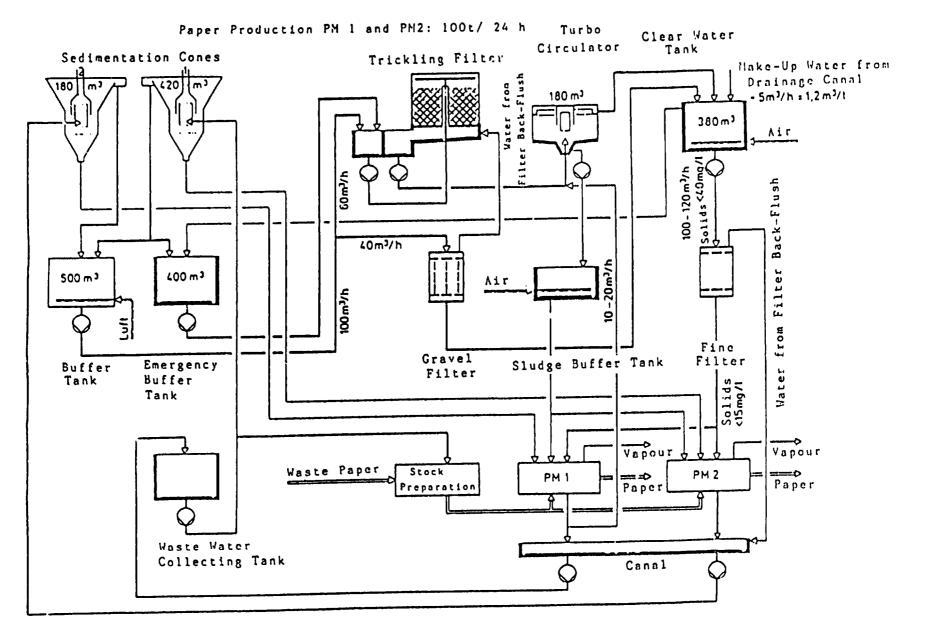
 G&P has developed the closed water cycle for waste paper processing. Table 27 shows the flow chart.

> Gissler & Pass Waste Paper Mill Postfach 2120 D-5170 Jülich contact: H. Boettcher

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<u>TABLE 27</u> (G&P closed Water Cycle for Waste Paper Processing⁽¹⁹⁾

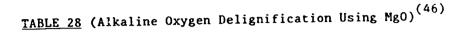
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3) Oxygen stages are rather well known in prebleaching kraft and conventional add-on processes. Ozone bleaching is being carried cut in a number of pilot plants, among them Swedish and German firms.

> contact: Dr. H. Klein Schwäbische Zellstoff AG Biberacherstrasse 73 D-7930 Ehingen/Donau



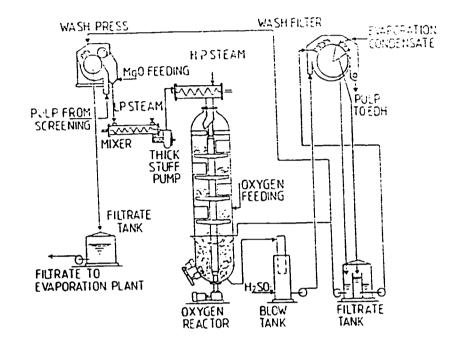
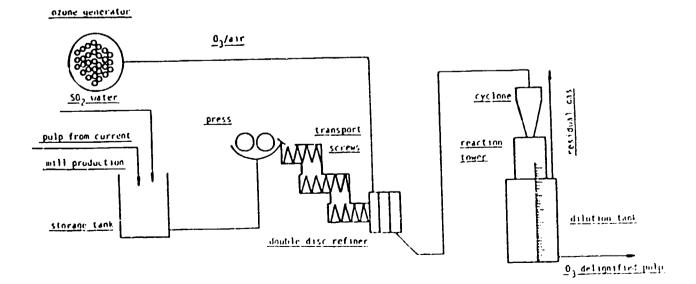
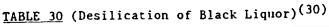


TABLE 29 (Pilot Plant for Ozone Bleaching)⁽⁴⁶⁾

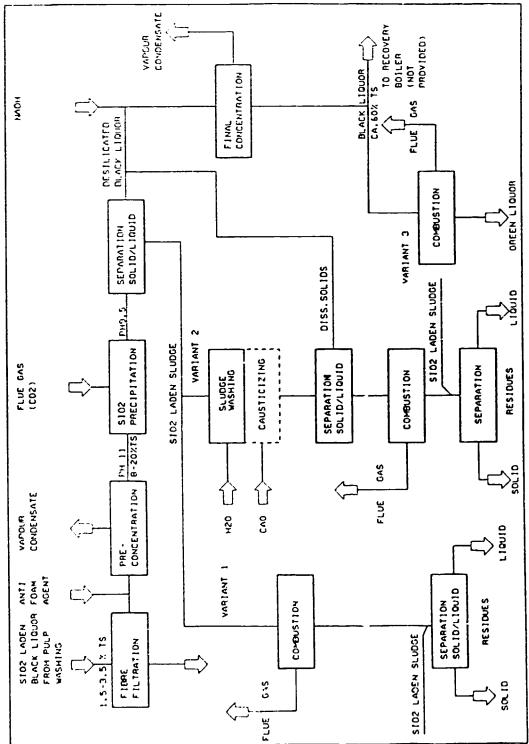


4) Desilication is being introduced to certain developing countries who use rice straw and other high silica containing raw material. Lurgi has achieved some remarkable results.

> contact: H. Schildham Lurgi GmbH Division of Inorganic Chemistry Gencinusstrasse 17-19 D-6000 Frankfurt/Main



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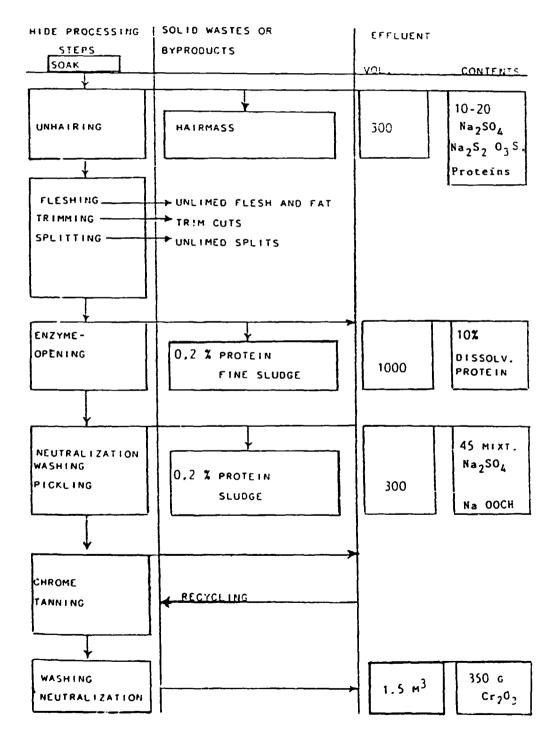


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TANNING
8.
     Remedial Environmental Technology:
     High chromium salt concentrations in the effluent (chrome tanning
     process only)
     High concentration of organics in the effluent of both processes
     (chrome and vegetable tanning)
     Large quantities of solid residues
     Centralized plants for Cr recovery
     Precipitation of Cr salts as hydroxides, storage as basic chrome
     sulphate
     Reinforcement and recycling of chrome baths
     Improved CR fixation
9.
    Preventive Clean Technology:
    Reuse of solid wastes
    - in the soap industry (fats)
     - in the carpet industry (tail, body hair)
    - in the manufacture of glue and gelatine
     - in the manufacture of leather boards, etc.
     - as fertilizer
     - as energy source, through biodegradation or incineration
     Darmstadt continuous flow method
```

ad 9: The Darmstadt flow method is less time consuming than other conventional beamhouse processes. To retrofit installations and techniques of yesterday and today will cost less or approximately the same as a new installation. CT produces, moreover, only a small fraction of effluent in respect of volume and load and of by-products in comparison with the conventional processes of ET.





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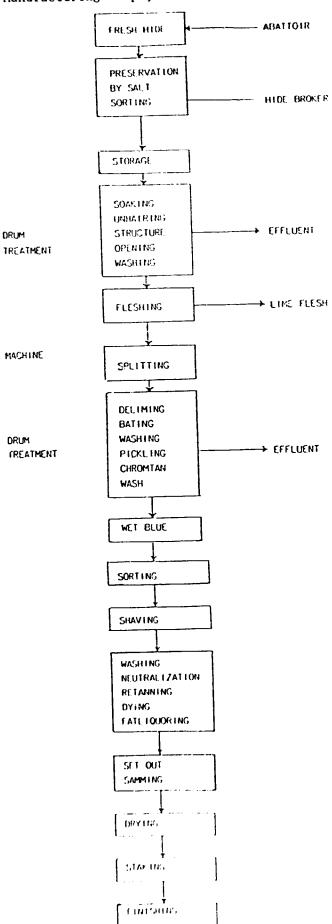
TABLE 32 (Leather Manufacturing Steps)⁽⁵⁴⁾

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TEXTILES

8. Remedial Environmental Technology:

Designing waste effluent is very strong in pollution material Biological treatment alone or in combination with sewage via activated sludge is feasible while chemical coagulation appears to be insufficient

9. Preventive Clean Technology:

Combine processes

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- combined designing and mercerizing
- combined designing and bleaching

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- combined designing, scouring and bleaching
- combined designing, dyeing and finishing

ad 8: Cotton mills: Substitute low-BOD synthetic detergents (syndets) (0 to 20% BOD) for soap (140 to 155% BOD). Substitution of steam ranges for oxidation of dyes, in place of dichromate-acetic acid baths (5 to 15% reduction). Use of less caustic in kierning (10 to 20% BOD reduction, 10 to 30% caustic reduction). Use of low-BOD dispersing, emulsifying, leveling, etc. agents in place of high BOD agents (5 to 15% reduction). The following inventory of process chemicals and BOD in woolen-mill wastes illustrates the situation also for cotton mills.

	Chemical composition	Usc	% OWF used*			1	BOD.	
Process chemical			Scouring and carding	Finishing	Total	Concentra- tion in effluent, ppm	% owc	% OWF
Soap	Fatty-acid soap	Scouring, fulling	2.1	5.5	7.6	152	155	11.7
Soda ash	Na.CO,	Scouring, fulling	14.2	2.8	17.0	340	0	0
Quadrafos	Na,P.O.	V'ashing		0	0.5	10	0	0
Pine oil	Pine oil	Washing	0.5	0	0.5	10	108	0.5
Paragon 500	?	÷	0.5	0	0.5	10		
Proxol T	Mineral oil, plus nonionic emulsifier	Carding	0.5	0	0.5	10	20	0.1
Acetic acid, 84%	CH,COOH	Dycing		1.2	1.2	24	62	0.7
Olive sub C3	Oil	Spinning	0.4	0	0.4	8		
Sulfuric acid	H,SO,	Carbonizing, dycing	0	0.2	0.2	4	0	0
Chrome mor-					ļ			
dant	$Na,Cr,O, + (NH_{*}),SO_{*}$	Dyeing	0	0.4	0.4	8	0	0
Chrome	Na,Cr,O,	Dyeing	0	0.6	0.6	12	0	0
Glauber salt	Na,SO,	Dyeing	0	0.4	0.4	8	0	0
Monochloro-					1	•	[1
benzene	C,H,CI	Dyeing	0	0.2	0.2	4	3	0
Nopco 1656	Soluble fatty ester	Spinning	0	0.2	0.2	4	12	0
Iversol	Blend of soaps, solvents, and detergents	Washing	0	1.6	1.6	32	60	1.0
Rinsol	Detergent	Washing	0	2.9	2.9	58	72	2.1
Supertex E	Fatty-acid soaps,	Washing	0	0.2	0.2	4	25	0.1
•	solvent cresylic acid			}	1	[[ĺ
Wool finish B	High carbohydrates and enzymes	Finish	0	2.3	2.3	46	57	4.3
	Added impurities							
	(subtotal) Natural impurities		18.7	18.5	37.2	748		17.5
	(grease, suint, dirt)	}	150.0	0	150.0	3000	167	250
	Grand total		168.7	18.5	187.2	3748	1 10./	-2.0
			100.7	10.5	101.2	3/40		42.5

TABLE 33 (Process Chemicals and BOD in Woolen Mill Wastes)⁽³³⁾

ad 9: There is an increased demand for textiles around the globe and especially in developing countries. Large as well as small textile mills are producing cotton, wool and/or linen as well as textile blends such as cotton/polyester, wool/polyacrylic, wool/polyamide, wool/polyester. The mills are old fashioned in the most part; high water and energy consumers. In general 1 kg of the loomstate fabric consumes 20-60 m³ of water to bring it up to the final product.

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Postscriptum

Environmental pollution by unmanaged chemicals and wastes contributes to deforestation, soil impoverishment, diminishing water supplies and desertification. These are alarming prospects! CT can contribute to thwarting these serious threats to living conditions in various parts of the developing world; not to speak, promote a new quality of life in the Third World.

I like to conclude with quoting the author of <u>Making Peace with the</u> <u>Planet</u>, Prof. Barry Commoner (Queens College Center for the Biology of Natural Systems, New York): "Don't 'control' pollution; prevent it".

"Earth Day 1990 is a turning point in the history of the environmental crisis. The crisis began with the end of World War II, when new technologies took over the major sectors of production. Agriculture became heavily based on chemicals. Cars became larger and more powerful. Nuclear power was introduced. Trucks replaced railroads. Plastics and other synthetic chemicals pushed natural materials out of the market.

This brought on the crisis. Chemicals leached from farm land, polluting water and our bodies with toxic substances. The big cars belchei smog and acid rain. Nuclear power gave us Three Mile Island, Chernobyl and the still-unsolved problem of radio-active waste. Trucks which burn four times as much fuel as railroads to move the same freight, have worsened air pollution. Plastics have cluttered the landscape, and toxic chemicals have accumulated in our bodies.

Since 1970, the United States has spent some \$1 trillion of public and private money trying to mop up the mounting wastes of the postwar technologies - guided by elaborate regulations, burgeoning bureaucracies and numerous court cases.

Now we can judge the result of this massive 20-year effort: It has failed to accomplish what it set out to do. For example, the EPA expected its automobile exhaust controls to reduce carbon monoxide emissions by 80% between 1975 and 1985. Instead, they fell only 19%. Nitrogen oxide emissions were supposed to decrease by 70% but actually increased by 4%.

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This pattern of failed expectations is widespread. With one key exception - lead - the annual emissions of air pollutants - carbon monoxide, sulfur dioxide, nitrogen oxides, dust and volatile organic compounds declined by an average of only 18% between 1975 and 1987. Pollution levels at nearly 90% of the river sites studied by the U.S. Geological Survey has deteriorated or remained the same. In the last 20 years, spills of oil and hazardous waste have become larger and more numerous.

Only a handful of pollutants have really been rolled back - by 70-90% since the early 1970s. Lead, DDT and PCBs are examples. These few successes tells us what works. In each case, the pollutant was simply eliminated from the technology of production. Lead has been largely removed from gasoline production. DDT, once chiefly used in cotton production, has been banned. PCB, also banned, is no longer used in the production of electrical equipment or paint. What has not worked is the effort to reduce pollution by tacking control devices on cars, power plants and chemical factories without otherwise changing them. There is a lesson here. Environmental pollution is an incurable disease. It can only be prevented. Prevention means not producing waste in the first place, which does away with the costly and futile cleanup. Prevention means zero levels of pollutants, elimnating the endless haggling over how much is "acceptable". Prevention means at last restoring our ailing environment to health". DATA SOURCES AND RESOURCES

For ET and CT the data sources are beginning to be available and are beginning to be offered by various services to both the practitioners and the researcher.

Two key publication help further to unravel this novel field.

Agnes Ottahal, <u>Umwelt-Datenbank-Führer</u>, Verlag TUV Rheinland, Koln, 1989, 370 pp, p.b.

United Nations, <u>ACCIS Guide to United Nations Information Sources</u> on the Environment, New York, 1988, 141 pp, p.b.

IACT (International Association for Clean Technology) is currently the only group specifically concerned with establishing a consulting and expert service, as well as a data base for CT.

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PHAST is one of the most recent and most sophisticated programs available. PHAST (Technica International, US dollars 27,500, Gircle 302) is a consequence analysis program capable of modelling a range of scenarios for accidental release of hazardous materials. It is suitable as an advanced screening tool for quantification of potential hazards within process plants. The program which combines an integrated set of fluid discharge, dispersion and flammability models with complex event trees, is derived from the company's quantitative risk analysis program SAFETI. A thermophysical properties database from the Design Institute for Physical Property Research of the American Institute of Chemical Engineers is included. PHAST runs on IBM XTs, ATs, PS/2s and their compatibles.

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