Hazardous waste

Introduction and special information for

Metal working industries

Agrochemical industries

Manufacture of paper and board

Fibrocement industries

Foreword

Fast economic growth is a generally accepted aim in politics and society. Increasing welfare can not be reached without economic success. But economic and industrial growth has also it's dark side. It is linked with environmental degradation and diminishing natural resources. Thus, economic activity can influence welfare, also, negatively. So, it is increasingly important to consider also, this negative impact of economic growth on the environment. One environmental issue is the generation and treatment of hazardous waste.

Hazardous materials emerge as waste and as by-product in many industries and sometimes old worn out products contain hazardous substances. The dangers of these substances are often not fully recognised. The absolute amount of hazardous waste is rather small compare to other waste. Furthermore, dangers of hazardous waste emerge often, only, in the long run e.g. through spoiled groundwater or through bioaccumulation. Hazardous substances can lead to diseases like cancer or are sometimes mutagenic . These negative effects emerge probably, only, years after exposure and hence, it is difficult to find a link to the real reason for a health or environmental issue. So, problems of hazardous waste are often underestimated because, dangers are difficult to perceive and long run costs to society are higher than expected.

This booklet may help to understand the issue of hazardous materials and wastes, better. It will give some basic information about the characteristics of hazardous materials, dangers and protection measures. It contains also, some information about handling, labelling and storage. Thereby, this booklet concentrate on some most relevant hazardous substances. This general introduction to hazardous waste issue is extended further by an overview of industry-specific tips.

For further detailed information consult us at our web-page www.sacodi.tu-dresden.de. There you will find a more comprehensive handbook and links to other interesting web-pages and literature.

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This document has been produced with the financial assistance of the European Union. The contents of this document are the sole responsibility of Partners of SACODI Project and can under no circumstances be regarded as reflecting the position of the European Union.

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General aspects of hazardous waste handling

§ Some remarks to the legal framework and business issues

Legislation on hazardous waste is, necessary, to protect the society from the dangers of hazardous materials. It is necessary to improve the standards of living and, to ensure reasonable living conditions. A developed society with an increasing industrialisation deserves a sophisticated environmental and hazardous waste legislation.

But companies usually, do not like these laws because they impose often, costs and reduce profits. Therefore, the companies try to circumvent such legislation by legal or illegal means. But, nevertheless, there are several arguments how, also, a company benefits from a strict hazardous waste legislation:

- Compliance of rules protect the health of the workers. The workers are more satisfied and therefore, can work better and, be more productive.
- Following the rules increases the reputation of a firm. It may, even, be, necessary to sell the products. Especially for selling abroad it is often necessary to meet certain environmental standards (e.g. ISO 14 000).
- Observing the laws reduces risks of liability suits e.g. from workers, affected neighbours or the government. Long run business risks will be reduced.
- Obeying the rules protects yourselves and your children from hazardous substances now and, reduces further risks in the future.
- An enforced legislation confront all companies with the same level playing field.

This shows that, proper waste management brings some advantages to firms. Therefore, an avoidance of good practice just, to save some costs is rather, short-sighted. Because, often, some investment is necessary and the best is, to plan long time in advance to determine economical and environmental efficient solutions. One basic principle for that, is the hierarchy of waste management. It gives a ranking of actions to tackle the issues on waste.

Hierarchy of waste management

Reduction and avoidance of waste

This is the first and the most important strategy of waste management. This approach is the most preferable and, is, a base for sustainable development. It can be done by altering the production technology or, sometimes, even by using some other product design. Any change in production

technology should seek to reduce the amount and the hazardousness of waste. Waste reduction is also possible through manufacturing of longer lasting products.

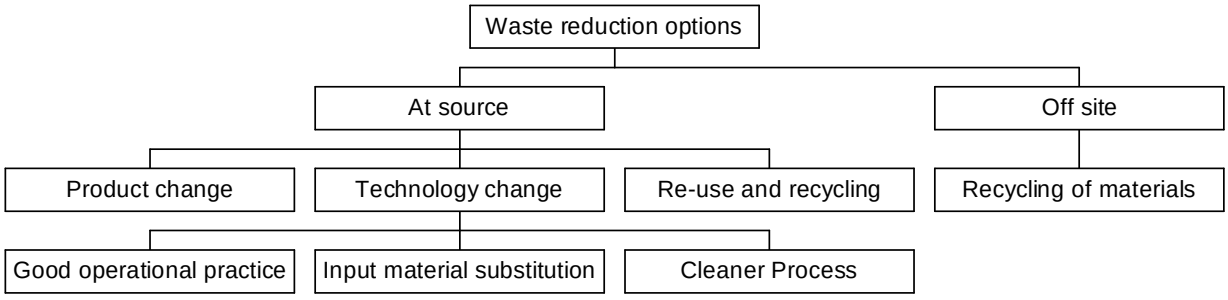
Waste reduction has a big advantage that, it helps to reduce input of raw materials or energy and to reduce the waste disposal costs. These savings have a direct positive economic effect on business and a long run positive effect on the whole society. So waste reduction can lead to a win-win situation it means, that, environmental damage can be reduced and at the same time costs can be lowered.

Re-use

In some cases, it is possible to re-use materials. This can be, also, economically beneficial. Re-use depends upon the properties of the material and the costs to make the material again available in terms of energy costs, cleaning, transportation etc. Re-use involves usually, some costs to clean the waste, to transport the waste to another user but, it helps also, to reduce disposal costs and costs of raw materials.

Recovery or Recycling

With some materials, recycling or recovery from waste is technically possible. If, this is practically feasible depends upon different factors. On one side there must be a market for the recycled materials. So availability and price of raw materials and quality of the recycled material are important. On the other side, recycling involves costs of proper collection which avoid mixing, transportation and recycling. But, sometimes, it causes even, environmental pollution, other waste and energy consumption so that, the overall environmental balance is not positive. Theoretically, the potential for recycling is high, practically, it is constrained through many economical and environmental factors. Recycling needs, often, political support to set a proper economical framework.



Disposal

This is the least preferred option of waste treatment. Sometimes, it is unavoidable due to technical or economical reasons. The aim, should be to find technical solutions, that reduce the dangers which emanate from disposal.

Dangers of hazardous materials and waste

Hazardous materials can cause different dangers. These dangers mainly come under three groups:

- All sorts of physical hazards, e.g. corrosive, inflammability, oxidising
- Health hazards, e.g. (toxicity by ingestion, inhalation or skin absorption, irritant)
- Environmental hazards, e.g. (soil and water contamination, negative impacts on flora and fauna)

Physical hazards are direct immediate risks and they can endanger humans and objects. Health hazards can have short or long term effects. Environmental hazards are often, long term issues and therefore, underestimated. On the following pages, some of the dangers of hazardous materials and waste are described. Some substances can have, several of the mentioned characteristics. To most of the characteristics, a commonly used label is attached. It is strongly recommended to use these signs for labelling containers that contain some kind of hazardous substances. The signs give basic information about the dangers and so they help to reduce accidents and harm to humans and the environment. Labels give some basic information on handling and, on emergency actions.

Characteristics of hazardous materials

Explosive

Materials that can explode owing to friction, sparks, fire, movements, beats or other ignition source. Handle with extreme care. Some materials should be checked frequently for signs of deterioration and aging. These signs include "sweating" of a container, bulging, crystal formation around the cap, etc. Deteriorating explosive materials are potentially more dangerous to handle than new explosives.

Oxidising chemical

Materials that spontaneously evolve oxygen or other oxidizing substances at room temperature or with slight heating, or that promote combustion. Together with combustible materials there is a danger of fire or explosion. Oxidizing materials can speed up the development of a fire and make it more intense, cause substances that do not normally burn readily in air to burn rapidly, cause combustible materials to burn spontaneously without the presence of obvious ignition sources. Examples are nitric acid, chromic acid or peroxide. Handle with care and keep it away from flammable chemicals!

Flammable

Flammable materials are (flagged by the sign **F**) are liquids that have a flashing point below 21° C and, that are not extremely flammable. Solids that can be inflamed through a short contact of an ignition source and continue to burn. Flammable is also material

that develops together with water or wet air, extremely flammable gases, material that can be heated by themselves at normal temperature without additional energy and burns finally. Examples are many solvents or dust of many material in a high air concentration.

Extremely flammable

Material will are extremely flammable and are flagged by the symbol **F+** when they are liquids that have a flashing point below 0° C and a boiling point below 35°C or ignitable gases at normal temperature and pressure.

Toxic or Poisonous

Toxic materials harm humans by touching, breathing or when swallowed. Material's toxicity depends, usually, on the dose. But, even very small doses can be dangerous especially, after long term or repeated exposure. Symbols discern two classes: **T** toxic and **T+** very toxic. Some examples for poisonous hazardous materials are heavy metals that are found in many metal residues or pesticides.

Irritant or Harmful

This sign characterise material that causes danger to health. The sign **Xn** denotes harmful material. The sign **Xi** denotes material that is irritant to the skin to eyes or the respiratory system. Many substances can be irritant or harmful. It can happen even through a degreasing effect. Even, in households you can find harmful substances like, cleaning agents.

Corrosive

Corrosives are materials that can attack and chemically destroy exposed body tissues. Corrosives can also cause damage or even, can destroy other materials like metals. They cause damage as soon as they come into contact with the skin, eyes, or other materials. Most corrosives are either acids or bases. Everyone, who, works with corrosives must be aware of the hazards and how to work safely with them. So, the skin must be protected. Storage and transport of corrosive materials has to be done in special containers. Examples are common acids like hydrochloric acid, sulphuric acid, nitric acid, chromic acid, acetic acid or hydrofluoric acid and bases like ammonium hydroxide, potassium hydroxide (caustic potash) or sodium hydroxide (caustic soda). Dangers depend upon the concentration of the substance. Corrosive substances in low concentration are irritant.

Environmental hazard

Hazardous materials endanger, often, the environment. This danger can be direct or through long exposure to harmful substances. Concentration plays also, an important role in determining the environmental hazard of a hazardous substance. But, in a long run even at low concentration nature can be affected negatively by hazardous waste.

Carcinogen

Many hazardous substances can cause cancer. Even if in low dose, a long term exposure can be dangerous to humans. Examples are benzene or asbestos.

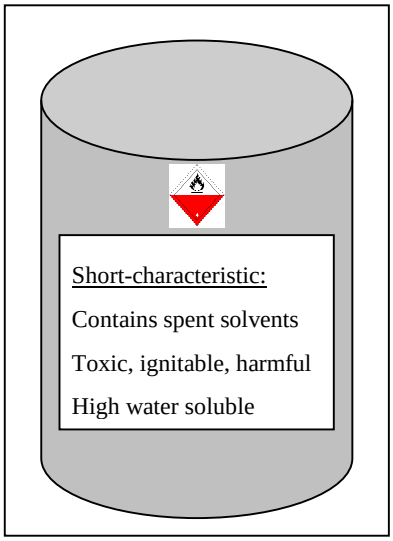
Mutagen

Hazardous materials can also change genetic information. The directly affected person may not even realise it. But their children will have different handicaps. Examples are nitrous acid, or sodium azide.

Handling of hazardous materials

Labelling

Labelling of hazardous materials is very important. It prevents false handling and in case of fire or spill or another emergency case it eases combat against hazards. Labels like “toxicity” or “ignitability” can show the risk caused to human health, the environment and the production process. So, the employees know how, they have to deal with the substances. In many countries official labelling systems exist. They are usually, based on the international classification system. Additionally, it is highly recommended to add some specific information. To optimise, there is, also, a short characteristic (compare the following illustration) of the substance recommended.



Storage and disposal containers

Containers holding hazardous material must be in a good condition, non-leaking and compatible with the waste being stored. Compatible means e.g. never store corrosive material in a metal container. The container must always be closed. Never mix incompatible wastes in the same container. If a container holding hazardous waste is not in a good condition, or if it begins to leak, the waste must be transferred from this container to a container that is in a good condition. A storage container holding hazardous material that is incompatible with any waste or other materials stored nearby must be

separated from the other materials or protected from them. So, e.g. keep water reactive materials like sodium away from water.

Handling

Some general rules that apply to all kinds of hazardous waste:

No smoking, no open fire: Many hazardous materials are flammable, explosive or develop volatile and flammable gases. Do not burn hazardous materials. It causes dangers for your health and the environment and it can cause risks like a fire outbreak.

Wear protective gloves, if necessary wear protective clothing, shoes and mask. Many hazardous materials are toxic or irritant.

Use sanitary facilities, especially washing facilities. Handling of toxic materials needs sufficient opportunities to clean oneself. When you are handling toxic or irritant substances, best is to, have an emergency shower. This diminishes negative effects of an accident.

Additional to these general rules, there are some specific rules that apply to certain characteristics of the hazardous material. In the table with the classification system, some special handling advice for certain material characteristics are listed.

Separation in the production process

Handling of hazardous materials is much easier with an optimised factory layout. Some basic rules are:

Have a special storage room for hazardous waste that fits to the characteristics of this waste (esp. dry, cool, fire proof, with a solid water proof floor). Furthermore, separate hazardous from non-hazardous waste. Only one person should hold the responsibility of the storage area for hazardous waste. The area should be clean, with impermeable base material, gas sensors and separated from the other parts of the company. Other requirements for such areas are, good ventilation or the existence of absorbent material. Also, there is the need for an emergency plan that is known to all persons working in that area. The following picture shows a schematic storage area in a company. Furthermore a regularly emergency training is highly recommended.

Install washing and sanitary facilities best between production area and social area. So before eating workers can clean themselves.

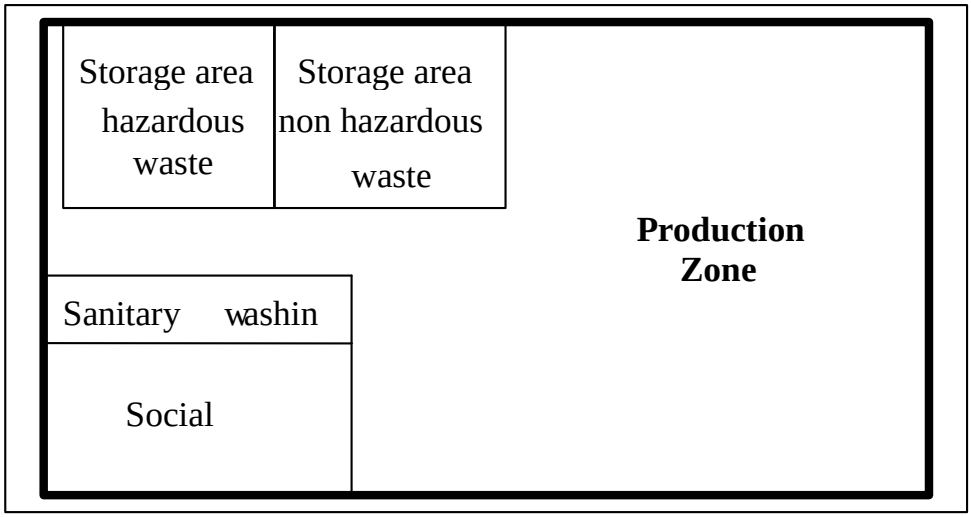


Figure 1 Layout of a storage area

Transport

Transport of hazardous materials has to be done with much care. Some rules are:

- Keep all existing road and transport regulation rules. Usually, there exist a comprehensive regulation for transport of hazardous materials.
- Inform the driver properly about the material and about possible danger so that he can avoid risks and that he has information for any emergency case.
- Equip the vehicle with a fire extinguisher.
- Label the vehicle and give the driver a detailed list with the substances. This is, especially, important in an emergency case. Depending upon the material, the combat against spills or fires needs special equipment.

First medical aid and emergency response

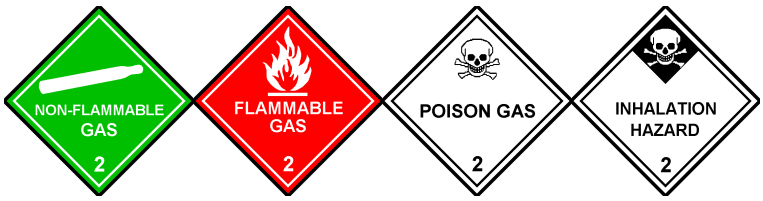
Some general rules that apply to hazardous materials:

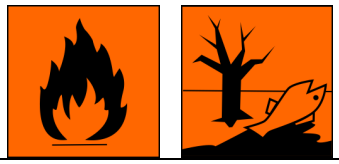
- After skin or eye contamination with harmful, irritant or toxic material, clean your skin or eye several minutes with a lot of water
- After burning your skin cool it, do not apply salve
- After swallowing drink a lot of water, if possible add active coal
- Consult immediately a doctor

Hazard Material Classification system

There is an international classification system of classification of hazardous materials. The following table gives an overview to it. Based on this system hazardous materials has to be marked by a sign that indicates most relevant properties and gives thereby basic information about characteristics of the material.

Class 1 Explosives	Will be omitted here because of low relevance
Class 2 Gases	
Class 3 Flammable liquids	
Class 4 Flammable solids; Spontaneously combustible materials; and Dangerous when wet materials/Water-reactive substances	
Class 5 Oxidizing substances and Organic peroxides	
Class 6 Toxic substances and Infectious substances	Class 6.2 infection substances is omitted here
Class 7 Radioactive substances	Will be omitted here because they require very special measurements and they are of low relevance
Class 8 Corrosive substances	
Class 9 Miscellaneous hazardous materials/Products, Substances or Organisms	

Gases Class 2 Compressed, liquefied, dissolved and toxic gases	
Examples	Flammable Gas: acetylene, butane, hydrogen, aerosols Non-Flammable Gas: oxygen, nitrogen Poisonous Gas: fluorine, chlorine, hydrogen cyanide, aerosols of low toxicity Sprays
Symbols	
Dangers	Explosion possible trough heat, fire or some other ignition source Dangers through leakage or poorly maintained containers Propane/butane is highly inflammable Waste can be water polluting
Safety	Do not crush container

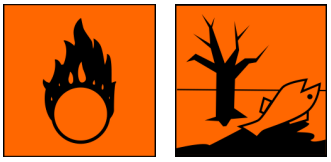
Flammable liquids Class 3 Possible additional dangers: Toxic, corrosive or explosive	
Examples	Paints, solvents, petrol, used oil, substances from pickling, hardener based on Isocyanate, acetone, ethanol
Symbols	
Dangers	Contain volatile compounds Vapour from solvents are heavier than air Used oil contains often, heavy metals Substances from pickling are highly corrosive Hardener based on isocyanate react with paint under production of heat Together with air they form explosive mixtures especially, in closed containers and rooms Vapour can be poisonous or can cause dizziness Many liquids spoil water and cause, thereby, damage to the environment

Flammable solids Class 4.1	
Examples	Sulphur, fat, wax, other solid waste containing flammable liquids, hydrocarbons, calcium carbide
Symbols	
Dangers	Oil contaminated substances can contain heavy metals Fire through heat, sparks or other ignition source possible, oil contaminated cloth can be self-inflammable waste can spoil water and cause, thereby, damage to the environment

Spontaneously combustible materials **Class 4.2**	
Examples	Phosphorus, chemicals from laboratories
Symbols	
Dangers	With oxidising materials strong chemical reaction possible Often toxic or development of toxic gases Self inflammable and danger of dust explosion waste can spoil water and cause, thereby, damage to the environment

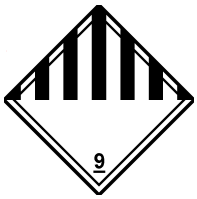
Safety for all flammable substances	Store in approved safety cans of cabinets Segregate from oxidizing acids and oxidizers Keep away from any source of ignition, such as flames, localized heat, or sparks Safety cans of drums containing flammable liquids should be grounded and bonded when being used Keep fire-fighting equipment readily available Have spill cleanup materials handy

Dangerous when wet materials/ Water-reactive substances **Class 4.3**	
Examples	Calcium carbide, sodium, aluminium phosphide, lithium
Symbols	
Dangers	React together with water explosive Can be heated by themselves Evolving gases are often, toxic and explosive waste can spoil water and cause, thereby, damage to the environment
Safety	Store in a cool and dry place In case of fire keep water away!

Oxidizing substances **Class 5.1 and** **Organic peroxides** **Class 5.2**	
Examples	Ammonium nitrate fertilizer, pool chlorine, hydrogen peroxide and other peroxides, potassium permanganate ,chemicals from laboratories, salts of sulphates, chromic acid
Symbols	
Dangers	Together with flammable materials they form explosive substances Sometimes even self inflammable Toxic and corrosive waste can spoil water and cause, thereby, damage to the environment peroxides can produce a lot of oxygen resulting in a potentially explosive situation
Safety	Keep away from flammable and combustible materials (including paper and wood) Store in a cool and dry place Keep away from reducing agents like zinc, caustics/alkalis and organic acids

Toxic substances **Class 6.1**	
Examples	Cyanide, arsenic, mercury and mercury containing waste, pesticides solid and liquids, halogenated solvents, methylene chloride (used as a paint stripper and a degreaser)
Symbols	
Dangers	Often volatile, toxic vapour! Combination with other dangers like flammability or explosive possible Even at low dose damage through long term exposure is possible Often carcinogen or mutagen waste can spoil water and cause, thereby, damage to the environment

Corrosive substances **Class 8**	
Examples	Battery acids, all acids and bases, mercury, potassium hydroxide, caustic soda, cleaning agents
Symbols	
Dangers	Often volatile, danger of corrosive, irritant or toxic vapour! Through mixture also, with water chemical reactions are possible that may create explosion waste can spoil water and cause, thereby, damage to the environment
Safety	Segregate bases from acids Segregate oxidizing acids from organic acids and flammable and combustible materials Segregate acids from bases and active metals such as sodium, potassium, magnesium Segregate acids from chemicals such as sodium cyanide, iron sulphide etc. which, may generate toxic gases upon contact Have neutralizers and solidifiers available in case of, acid spills or caustic spills

Miscellaneous hazardous materials/Products, Substances or Organisms **Class 9**	
Examples	Asbestos, electronic waste, batteries
Symbols	
Dangers	Some are carcinogen, Contain often heavy metals

Some industry specific information

1. Casting of Metals

Steps of the process

- *Pattern making and mould preparation*
  - A pattern is the replica of an original piece of work. Plaster, woods, plastics or wax could be used. After pattern creation, a mould is created.

- *Metal making*
  - Firstly, the scrap is prepared; metals are cut, cleaned and degreased. The following types of furnace are used – cupola, electric arc, reverberatory induction and crucible.

- *Shakeout, cooling and sand handling*
  - After melting, the metal is put into the mould and cooled. The material is then taken to the shake out area where the mould is replaced. The waste sand can be used several times; it is sieved first to remove pieces of metal; magnetic separation to remove ferrous parts can follow.
  - the sand can be used in construction, if, it can not be treated.

- *Quenching, finishing, cooling and coating*
  - Quenching (rapid cooling) in a bath is practised, after cooling and shakeout the casting process is finished by cleaning, sand blasting and steel shot blasting are used, if necessary. A negative aspect of quenching is, that there is an increase in the amount of wastewater

- *Die casting*
  - The dies consist of two blocks of steel, a hot die casting area (5000 psi) and a cold die casting area (10000 psi).

Waste reduction options

Good operation practises

- reuse of the mould for several years
- minimisation of adding harmful substances
- good practise is related to well trained personnel

Regeneration of sand

- Contaminated foundry sand often contains heavy metals and other harmful organic compounds. Thus, the sand needs to be treated. It can be treated in the following ways: cooling, crushing and sieving, cleaning by mechanical friction, wind sighting, high-pressure washing and incineration.
- Most of the above treatments are used only, in large factories due to cost. Options for small-scale industries are being developed.

Handling/disposal/prevention – general aspects

Please refer to next section

The table on the following page gives an overview on waste characteristics, probable risks and first steps to minimize these risks.

***Table 1**: Overview- casting of metals*

	Waste characteristics	**Probable risk**	**Steps to lessen risk**
Air Emissions	- fly ash, - metallic dust; containing nickel, lead, chromium, cadmium and zinc - air emissions	- associated issues with dust and ash inhalation.	- use of mould for several years - minimisation of adding harmful substances, - well trained personnel, - Improving the mixing tempera-ture as this prevents emissions and minimises hazardous compounds
Wastewater (Liquid emissions)	- cooling water - wet scrubber effluent - water containing oil and suspended solids	- exposure to skin and inhalation risks, - risk of damage to environment	
Solids	- dust from air cleaning, - slag containing heavy metals, - sludge in some cases containing corrosive substances, - casting sands containing cadmium or lead - waste oil, lubricants and other hydraulics	- exposure to heavy metals - exposure to skin and inhalation risks	Refer to next section with regard to details on handling, disposal and prevention of such wastes.

2. Metallurgical Industry

The four main processes in the metallurgical industry are, machining operations, cleaning and stripping, metal surface treatment and plating and paint application. The most important details on the waste characteristic, risks and first steps to reduce the risks in the sector of treatment metallurgical work pieces, are summarised in the table on the following page.

<u>The basic issues associated with wastes from metallurgical processes are:</u>

- A small fraction of any metallurgical waste is hazardous.
- This can lead to the waste not being recognised.
- Many dangers are due to the emission of volatile substances
  This may cause for example: water pollution or soil and groundwater contamination.
- Imminent dangers to employees arise especially from volatile chemicals and aggressive liquids.
- Basic strategies for reduction should include recycling of metal scrap and residues, reduction of chemical use and the substitution of hazardous chemicals with less harmful options.

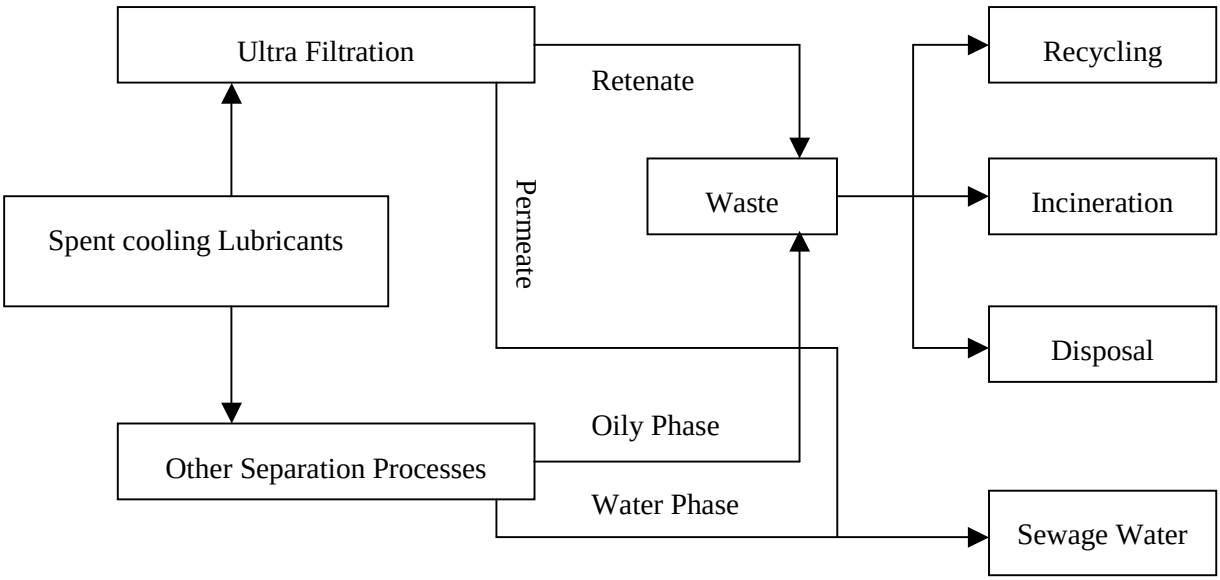


Figure 2: Waste streams from spent liquids

Table 2: *Overview- metallurgical industry (part 1)*

	Waste characteristics	**Probable risk**	**Steps to lessen risk**
Machining operations (wastes from shipping)	Metal working fluids, contain the following: - Oil - Emulsifiers - Anti weld agents - Corrosion inhibitors - Extreme pressure additives - Buffers - Biocides	- Hypersensitivity - Pneumonitis - Chronic bronchitis - Impaired lung function - Asthma	Waste reduction through: - Working fluids management - Avoidance of working fluids - Selection of working fluids - recycling
Cleaning and stripping (wastes from metal degreasing, machinery maintenance, water and steam degreasing and mechanical surface treatment)	- Halogenated solvent waste - Halogen-free solvent waste - Blasting grit - Waste of abrasive cleaning processes - Waste containing aliphatic hydrocarbons and ketones	- Highly volatile, damaging to ozone layer - Volatile, irritating, flammable - Metals (including lead and copper) - Paint, heavy metals, sodium bicarbonate, aluminium oxide - Solvents, oil, grease and tar	- Avoidance of cleaning - Minimising vapour loss - Maintaining solvent quality - Alkali degreasing - Solvent recycling - Improving collection efficiency

***Table 3**: Overview- metallurgical industry (part 2)*

	Waste characteristics	**Probable risk**	**Steps to lessen risk**
Metal surface treatment and plating (Liquid wastes from sludge from metal treatment and coating, Sludge and soils from tempering process)	- Spent bath solutions and filter sludge - Spent bath salts - Wastewater treatment sludge - Fractions of heavy metals (chromate and cyanide)	- Heavy metals, cyanides, additives, phosphates Metals, fluorides, cyanide and acid in sludge - Corrosive, cyanide - Heavy metals, acids	- Reduction of rinse water consumption - Change of bath composition - Alternative technologies - Bath regeneration - Prevention of spoils of salt baths - Alternative for nitriding and carburising - Optimising of quenching
Paint application (Wastes from manufacture, formulation supply and use of paint)	- Dependant on solvents and pigments - Pigments contain (chromium, molybdenum, cadmium, lead)	- Exposure to heavy metals - Exposure to solvents - Exposure to pigments	- Use of alternative paints to prevent sludge containing solvents - Alternative application - Reduction, catching and reuse of overspray

3. Chemical and Agrochemical Industry

Fertiliser industry

The following fertilisers can be used as straight or complex fertilisers:

- nitrogen fertilisers,
- phosphate fertilisers,
- potash fertilisers,
- Multi nutrient fertilisers.

Manufacture of N (nitrogen) fertilisers

Urea – this occurs at temperatures between 180º and 190ºc as well as, under 140 -- 200 bars of pressure. Ammonium carbamate is formed and is followed by dehydration and to water and urea.

For the synthesis of Ammonium carbamate, the following processes are applied: carbon dioxide stripping, ammonia stripping, the advanced cost and energy saving process (ACES) and the isobaric double recycle process (IDR).

Urea ammonium nitrate

This is formed by mixing concentrated urea with ammonium nitrate. There are continuous and batch processes applied. Another possibility, is the use of unconverted NH_3 and CO_2 from the urea produced.

Ammonium and calcium-ammonium nitrate

Gaseous ammonia is used to produce ammonium nitrate and nitric acid is neutralised. If dolomite, calcium carbonate and ground limestone is added, a calcium ammonium nitrate fertiliser is created.

Manufacture of N (K, P, and S) – Fertilisers

Single and triple superphosphate

The main objective is the transfer of mineral phosphate to a water-soluble form. For single superphosphate, this is achieved with sulphuric acid, if phosphoric acid is formed, double or triple-superphosphate can be produced.

Multi nutrient fertilisers

This is possible by the dry mixing of mono-fertilisers. During production, processes that belong to mixed acid route sulphuric, nitric or phosphoric acids are mixed. Neutralisation is

achieved by the addition of gaseous ammonia. In the finishing process, the substances are dried, screened, cooled granulated or coated.

Fertilisers that are produced with the phosphoric acid route are, mono-ammonium phosphate, di-ammonium phosphate and NPK fertilisers.

Multi nutrient fertilisers can be produced with the nitric acid route, a secondary product is, calcium nitrate, which can also be used as a fertiliser.

Hazardous materials

The following wastes can be generated:

- asbestos,
- waste or used batteries,
- heavy metals,
- spilt chemicals,
- waste oils,
- Components like herbicides.

Characteristics of compound fertilisers

There is a risk of fire and explosion and ammonia is also toxic. Urea is a toxic hazard and, if it forms a gas mix, explosions can occur. Both urea and nitric acid can corrode operating systems. Nitric acid, is an explosion risk, if nitrate or nitrate salts are formed. Ammonium nitrate and calcium nitrate are oxidising agents.

Waste reduction options

The main source of waste reduction is:
reducing the amount of chemicals, that are used in the process.
Furthermore, it is necessary that the users of chemicals are trained appropriately.

Production of nitrogen fertilisers

Recycling and recovering of carbamate gases is important. A vacuum at the top of the prilling tower and improved operations in the baghouses and scrubbers can reduce this and also, air emissions.

In nitric acid plants, higher pressures and reduction of the temperature in the weak acid liquid in the absorber can increase the absorption of nitrous acid gases.

Production of phosphor fertilisers

Scrubbers can reduce the production of fluorine compounds. A recycling process can reduce the amount of scrubbing effluent. If this is not an option, the effluent can be treated separately, and the heavy metals be removed.

Production of mixed fertiliser products:

The forming of gases like NO_2 can be prevented by the addition of urea in the digestion stage. By scrubbers, it is possible to reduce emissions of ammonia.

Manufacture of pesticides

There are two phases:

1) development of basic pesticide active ingredients
2) fillers, inert ingredients, propellants and binders are added.

A distinction is drawn between the following types of pesticides:

- disinfectants,
- repellents,
- rodenticides,
- fungicides,
- insecticides,
- herbicides.

Hazardous materials

This involves the reduction of air emissions, prevention of effluents and solid wastes.

Air emissions – flue gas is to scrub, treatment by baghouses and carbon absorption is possible. If the levels of toxins are high, a combustion step can be used.

Effluents and solid wastes – filtration processes and ultrafiltration through osmosis are often used methods. After filtration, oxidation, biological treatments, flocculation and carbon absorption can be used.

Solid toxic wastes should be incinerated.

4. Manufacture of Paper and Board

Processes and waste

Paper production generates huge amounts of waste, the majority of it is not hazardous, bu, due to its large volume, can cause environmental damage.

Pulping

There are various types of pulping. The main task of pulping, is the separation of cellulose and the removal of impurities.

Chemical pulping, wood fibre – a long fibre is produced, the wood is boiled in a mixture containing sodium hydroxide and as a result, sulphite pulp is produced. Other chemicals used, include sulphuric acid and hydrogen sulphite.

Mechanical pulping, waste fibre – waste paper from paper production, the publishing industry and used paper from households are used. Caustic soda, aluminium sulphate and dispersion agents are used in this process.

Chemo-mechanical pulping, waste fibre – for the higher quality fibre paper, de-inking is carried out. Detergents, dispersants and foaming agents are used for the separation of ink and fibre.

Mechanical/chemical pulping, non-wood fibre – non-wood fibres are annual crops, plants and residuals from agricultural production. The same methods as mechanical pulping of woods, are used, but in contrast, organic solvents are used such as alcohol and potassium hydroxide.

Bleaching

Hydrogen peroxide brightening – used for mechanical pulp with a high level of lignin. The change results in a lighter structure in the pulp. The lignin is left in the pulp and energy consumption is, also, high.

Chlorine bleaching – in contrast to hydrogen peroxide bleaching, chlorine gas is used to remove lignin. As well as chlorine, hazardous chlorine dioxide and hyperchlorite are necessary and organochlorines are a possible by-product.

TCF (total chlorine free) bleaching – delignification takes place with peroxide brightening with the help of enzymes. A chelating agent, like ETDA, prevents the decomposition of hydrogen peroxide.

ECF (elemental chlorine) bleaching – This process uses oxygen in the first stage, and chlorine dioxide in the latter stages. Caustic soda, oxygen and hydrogen are also used.

Paper production

Layering/bonding – this is the next stage in the paper production process. Water is removed from the pulp and the fibres are bonded to a web of paper.

Forming – here, the paper is pressed, dried and brought into length; this is often combined with the coating process.

Coating – this process leads to an improvement of writing or printing quality. It is necessary, because raw paper soaks up water. Polymers, like starch are added in the 'sizing' process and latex, binding agents, kaolin or calcium carbonate are added, to increase smoothness.

Finishing – this is a dry process, it also includes trimming, cutting and the continuous preparation for sale.

Waste streams

The largest volumes of wastewater are not hazardous, and, hence, can be treated with a simple waste water treatment process. Hazardous components are found in the following:

- spent halogenated solvents,
- corrosive waste from acids and bases,
- paint waste containing solvents and heavy metals,
- ink waste with solvents, heavy metals and ignitable materials.

Hazardous materials

Chemical pumping process – sodium sulphate, acid sulphate and bisulphate and alkaline waste like spent sodium hydroxide.

Bleaching – toxic wastewater, wastewater treatment sludge, acid and alkaline waste is generated.

Paper manufacture – wastewater, wastewater treatment sludge, toxic waste including added chemicals, spent solvents, ignitable waste and toxic rinse water.

The waste streams may, contain any of the following: carbon tetrachloride, methylene chloride, tetrachloroethylene, 1,1,1 trichloroethylene, trichloroethylene, chloroform, benzene, ethylene dichlonde, chlorobenzene, methyl ethyl ketone, dioxins, furans and other halogenated compounds.

Hazardous waste reduction options

1) Optimisation of de-inking process. Fibres of a sufficient length can be reused by a pressure screening process. Separation by flotation, where air is added to the sludge and the ink rises to the water surface and thus, can be removed. Enhanced cellulose filtration called TUROSCREEN can be used.

2) Use of non-metal containing inks. Resin based and oil based inks can be used. The separation of the fibres and ink requires fewer chemicals. Water based inks for newspapers have been tested successfully.

3) Recycling of coating colours. This can be achieved by membrane technologies; however, these technologies are expensive and not viable for small companies.

Handling/disposal/prevention – general aspects

The first step, should be a data collection of all substances, chemicals and wastes in the company. The following step, should be a search and identification of alternative non-hazardous chemicals. Educating the employees is also necessary.

Regarding storage, hazardous waste, should always be kept separate from the household and non hazardous waste. It should, then be easier to treat or dispose of the hazardous compounds with an environmentally sound method.

All equipment should be free of leaks or other damage.

Fibre costs can be lowered by the application of waste paper to the de-inking process. The recovery of other chemicals is possible in a looped system.

Other techniques for waste prevention are as follows:

- Adoption of the water use and waste water system to the local climate as well as technical and economic requirements,
- Application of chlorine-free bleaching methods, and
- Prevention of forming dioxins and furans from chlorine bleaching.

5. Production/ Application of Fibrocement

Process description

The manufacture of fibrocement starts with the grinding of the asbestos. It is then, mixed with water and then cement. During the finishing stages, the material is cut.

Hazardous materials

Asbestos contains the following substances:

- chrysotile,
- amosite,
- crocidolite,
- tremolite,
- anthophyllite,
- actinolite.

They all, consist of a magnesia silicate; they have a crystal structure with diameters ranging between 3 and 20 micrometers. Crocodilite is the most dangerous type of asbestos.

Asbestos is classifieded as a hazardous substance because, it can cause asbestosis (a chronic lung disease) and mesothelioma (tumour of the lung).

Waste reduction options

This refers to the prevention of products containing asbestos and the substitution of asbestos fibres in the production of fibrocement. The following alternatives have been developed:

1) Manufactured inorganic fibres – the purpose of these non-hazardous fibres, was to develop a fibre with a diameter too large to enter the lungs. For a long time, the glass fibre, was thought to be an alternative. However, further research determined that, it could be inhaled. Glass and stone wool products are used instead and to handle materials, like asbestos.
2) Naturally occurring crystalline fibres and other materials – examples are wollastonite and perlite which can be used. They are not breathable and can damage the lung. The handling is the same for manufactured inorganic fibres.
3) Naturally organic fibre – these are based on cotton or cellulose, they can, however, be harmful to the lungs and should be treated with care.

4) Manufactured organic fibre – Kevlar, polyvinylalcohol (PVA) and polystyrene are manufactured organic fibres that, are used as an alternative to asbestos. Kevlar and PVA are less likely to cause lung cancer than asbestos, polystyrene gives off toxic fumes, if heated.

Handling/disposal/prevention- general aspects

It is always appropriate to wear a protective mask, hats, gloves and overalls. A shower, should be taken after exposure to asbestos.

During destruction of asbestos containing materials, a vacuum cleaner should be used to minimise fibre spread. The bags from the vacuum cleaner should be disposed of separately to the household waste. The bags should be sealed and not reused.

In the storage room of asbestos, all necessary information concerning risks of exposure, the origin of the waste and the person responsible, should be visible.

Transport should ensure, that there is no spillage.

With regard to fibrocement, all fibre emissions are to be collected and workers should wear protective clothing.

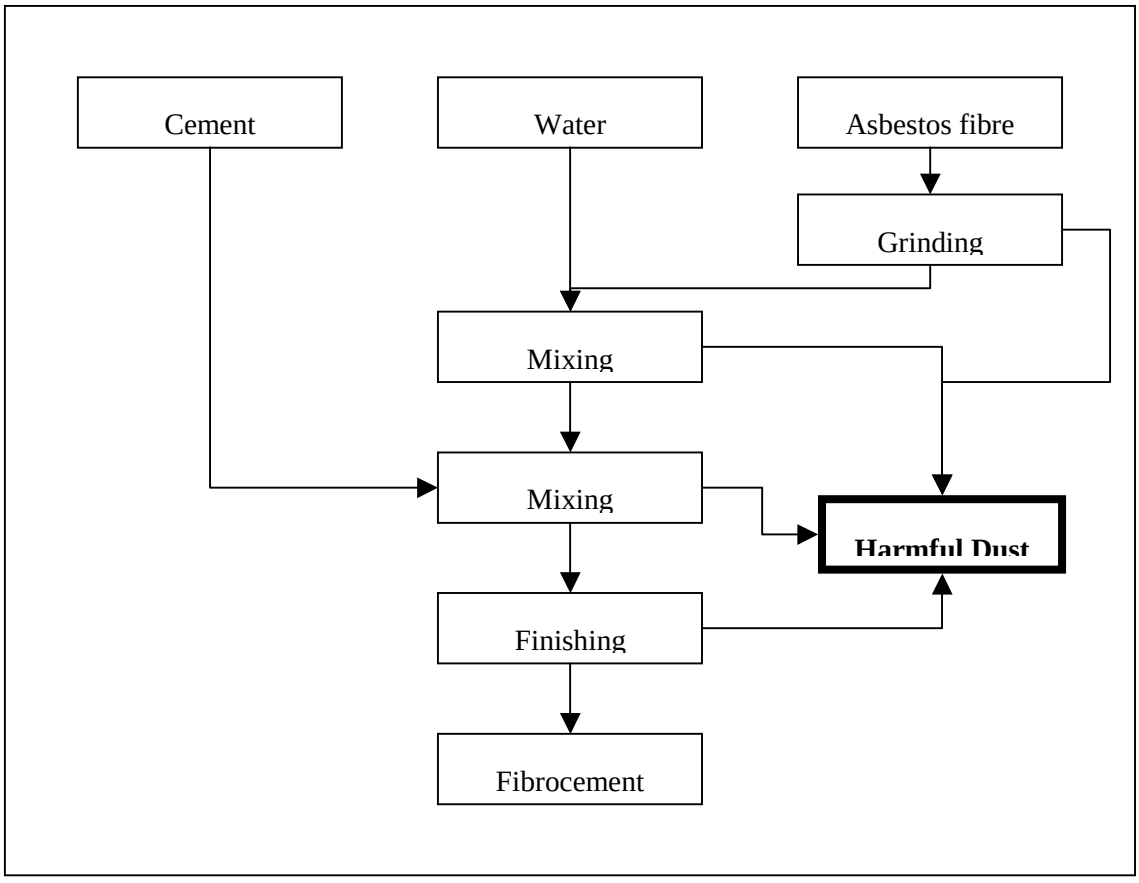
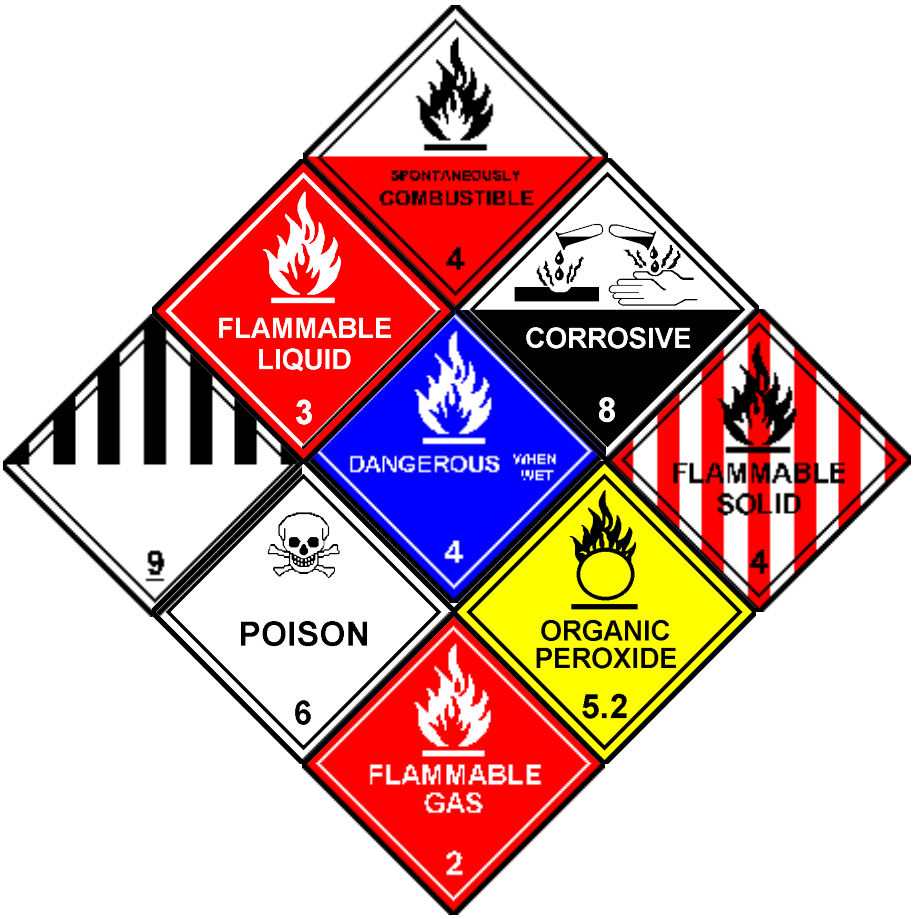


Figure 3: Dangers of Fibrocement production



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