IAMC Toolkit

Innovative Approaches for the Sound Management
of Chemicals and Chemical Waste

Technical Manual

Synthesis of Polymers

July 2016

Masthead

Publisher: UNIDO, Environmental Management Branch, Vienna

Authors: CSD Engineers, ISSPPRO

Unless otherwise mentioned, all references to sums of money are given in United States dollars. References to “tons” are to metric tons, unless otherwise stated.

Contents

1 Introduction

The United Nations Industrial Development Organization’s (UNIDO) overarching objective is to reduce poverty through sustainable industrial development. In response to this global challenge, UNIDO launched the ***Green Industry*** initiative with the aim of fostering the positive role of industry in achieving sustainable economic growth. According to UNIDO’s Green Industry vision, the industries’ role is to constantly provide creative and innovative solutions and alternatives to countries’ economies, focusing on a well-balanced economic, environmental and social impact of industry. Sustainable development has indeed become a core determinant of economic competitiveness and allows industries to decouple their economic growth and revenues from excessive and increasing resource use and pollution by minimizing waste in every form, using renewable resources, taking precautions to avoid harming workers, communities as well as the environment [1].

The joint global ***UNIDO-UNEP Resource Efficient and Cleaner Production (RECP) Programme*** endorses the Green Industry vision. The programme is based on a multi-pronged programmatically and geographically focused approach to scale up and mainstream the application of RECP concepts, methods, techniques, technologies and policies in developing and transition countries in order to improve resource efficiency and environmental performance of enterprises and other organizations, in particular small and medium-sized operators in the manufacturing and associated sectors.

The multi-faceted reliance on chemicals across industries makes chemicals production one of the major and most globalized industrial sectors with a high impact on the overall sustainability performance of supply chains. The essential economic role of chemicals and their contribution to improved living standards needs to be balanced under consideration of all potential costs. An adequate cost analysis thus has to include the ***chemical industry’s use of resources,*** such as water and energy, and the potential adverse impacts of chemicals on the environment and human health. The potential severity and complexity of such impacts highlights the fact that sound chemicals management is a key issue for sustainable development [2].

Under this programme, the project entitled ***Innovative Approaches for the Sound Management of Chemicals and Chemical Waste*** aims at providing three groups of industries, namely producers of chemicals, formulators and industrial users of chemical products, with innovative approaches and specific technical solutions to chemicals and chemical waste management. The main target is to achieve a reduction of chemical consumption in both production and application of chemicals. Further targets also address the replacement of hazardous chemicals by chemicals with a lower risk, the reduction of chemical wastes, the safe handling of chemicals and risk reduction related to accidents with chemicals. In each of the five participating countries (as of 2013: Colombia, Egypt, El Salvador, Morocco and Peru) and the three groups of industries concerned by the project, the identification and implementation of innovative alternatives and solutions is made on a subsector basis (i.e. industries in the paint formulation, paint application, textile finishing and polymers domains). Assessments in subsectors in each of the participating countries led to the development of the present ***technical manual***, which aims at triggering innovative ideas, providing cost-effective innovative solutions and at enabling companies in these countries and subsectors to implement environmentally sound management of chemicals and chemical waste with high impact.

Introducción

El principal objetivo de la Organización de las Naciones Unidas para el Desarrollo Industrial (ONUDI) es reducir la pobreza por medio del desarrollo industrial sostenible. En respuesta a este desafío global, ONUDI lanzó la iniciativa ***Industria Verde*** con el objetivo de promover el papel positivo de la industria a la hora de conseguir un crecimiento económico sostenible. Según la visión de la Industria Verde de ONUDI, el papel de las industrias es el de ofrecer constantemente soluciones y alternativas creativas e innovadoras a las economías de los países, centrándose en un impacto social de la industria bien equilibrado, económico y medioambiental. De hecho, el desarrollo sostenible se ha convertido en un factor decisivo central de la competitividad económica y permite a las industrias separar su crecimiento económico y sus ingresos del uso de recursos excesivo y creciente y de la polución, así como minimizando el gasto en todas las formas, usando recursos renovables, tomando precauciones para evitar dañar a los trabajadores, así como a las comunidades y al medioambiente [1].

El ***Programa ONUDI-PNUMA para la Eficiencia en el uso de Recursos y Producción Más Limpia (RECP)*** respalda la visión de la Industria Verde. El programa está basado en una estrategia multidual con enfoque programático y geográfico para aumentar y hacer prevalecer la aplicación de los conceptos, métodos, técnicas, tecnologías y políticas RECP en los países en desarrollo y en transición. El objetivo es de mejorar la eficiencia en el uso de los recursos y el rendimiento medioambiental de las empresas, con especial enfoque a los medianos y pequeños operadores de los sectores manufactureros y asociados.

La interdependencia de las industrias en relación con las sustancias químicas a lo largo de las industrias hace que la producción de sustancias químicas sea uno de los mayores sectores industriales y más globalizados con un alto impacto sobre el rendimiento global de la sostenibilidad de las cadenas de suministro. El papel económico esencial de las sustancias químicas y su contribución a la mejora del nivel de vida debe ser equilibrado considerando todos los costes potenciales. Así, un análisis de costes adecuado debe incluir el **uso de recursos por la industria química** como el agua y la energía, así como los impactos potenciales adversos de las sustancias químicas sobre el medioambiente y la salud humana. Teniendo en cuenta la potencial severidad y complejidad de dichos impactos, subraya el hecho de que la buena gestión de las sustancias químicas constituye un factor clave para el desarrollo sostenible [2].

Bajo este programa, el proyecto titulado ***Enfoques Innovadores para una Buena Gestión de las Sustancias y de los Desechos Químicos*** pretende ofrecer a tres grupos de industrias, en concreto a los productores de sustancias químicas, a los formuladores y a los usuarios industriales de productos químicos, enfoques innovadores y soluciones técnicas específicas a la gestión de sustancias y desechos químicos. El principal objetivo es lograr una reducción del consumo de sustancias químicas tanto en su producción como en su aplicación. Además, se pretende afrontar la sustitución de sustancias químicas peligrosas por sustancias químicas de menor riesgo, la reducción de los desechos químicos y el tratamiento seguro de sustancias químicas y la reducción de riesgos relacionados con los accidentes con sustancias químicas. En cada uno de los 5 países participantes (en 2013: Colombia, Egipto, El Salvador, Marruecos y Perú) y en los tres grupos de industrias interesados en el proyecto, la identificación y la implementación de alternativas y soluciones innovadoras se realiza sobre una base subsectorial (es decir, industrias de formulación y aplicación de pinturas, acabado de textiles y polímeros). Las evaluaciones en subsectores en cada uno de los países participantes condujo al desarrollo del presente ***manual técnico*** que pretende desencadenar ideas innovadoras, ofreciendo soluciones innovadores efectivas a nivel de costes y permitiendo a las empresas y a los subsectores en estos países implementar una buena gestión medioambiental de las sustancias y desechos químicos con un gran impacto.

Introduction

L'objectif prioritaire de l'Organisation des Nations Unies pour le développement industriel (ONUDI) est de réduire la pauvreté à l'aide du développement industriel durable. Pour répondre à ce défi mondial, l'ONUDI a lancé l'initiative en faveur de ***l'industrie verte (Green Industry)*** dans le but de promouvoir le rôle positif de l'industrie dans la croissance économique durable. Selon la vision de l'industrie verte de l'ONUDI, le rôle des industries est de fournir en permanence des solutions et des alternatives créatives et innovantes aux économies des pays, en recherchant un équilibre entre les impacts économiques, environnementaux et sociaux. Le développement durable est en effet devenu un facteur déterminant de la compétitivité économique et permet aux industries d'assurer la croissance économique et les revenus, tout en limitant la pollution et l'utilisation excessive des ressources, en réduisant toutes les formes de déchets, en utilisant des ressources renouvelables et en prenant des précautions pour éviter de nuire aux travailleurs, aux communautés et à l'environnement [11].

Le ***Programme mondial commun de production propre et économe en ressources (PCER) de l'ONUDI-PNUE*** sanctionne la vision de l'industrie verte. Le programme est basé sur une approche à plusieurs volets dont les objectifs (en termes de contenu et de géographie) sont d'étendre et d'intégrer l'application des concepts, méthodes, techniques, technologies et politiques du PCER dans les pays en développement et en transition. Le programme vise à améliorer l'efficacité des ressources et la performance environnementale des entreprises et des autres organisations, en particulier les acteurs de petite et moyenne taille dans les secteurs de la production.

La dépendance multiple des industries vis-à-vis des produits chimiques fait de leur production l'un des secteurs industriels les plus mondialisés, générant un impact important sur la durabilité des chaînes d'approvisionnement. Le rôle économique essentiel des produits chimiques et leur contribution à l'amélioration du niveau de vie doivent être pondérés au regard de l'ensemble des coûts potentiels. Une analyse adéquate des coûts doit donc inclure ***l'utilisation des ressources par l'industrie chimique,*** comme l'eau et l'énergie, ainsi que les impacts négatifs potentiels des produits chimiques sur l'environnement et la santé humaine. Prendre en considération la gravité potentielle et la complexité de ces impacts, met en évidence le fait que la gestion rationnelle des produits chimiques est une question clé pour le développement durable [2].

En vertu de ce programme, le projet intitulé ***Approches novatrices pour la gestion rationnelle des produits chimiques et des déchets chimiques*** vise à fournir à trois groupes d'industries, à savoir, les producteurs de produits chimiques, les formulateurs et les utilisateurs industriels de produits chimiques, des approches novatrices et des solutions techniques spécifiques pour la gestion des produits chimiques et des déchets chimiques. L'objectif principal est de parvenir à une réduction de la consommation de produits chimiques tant dans leur production que leur application. D'autres objectifs portent également sur le remplacement des produits chimiques dangereux par des produits chimiques moins risqués, la réduction des déchets chimiques, la manipulation en toute sécurité des produits chimiques et la réduction des risques liés aux accidents avec des produits chimiques. Dans chacun des cinq pays participants (depuis 2013 : la Colombie, l'Égypte, le Salvador, le Maroc et le Pérou) et des trois groupes d'industries concernés par le projet, l'identification et la mise en œuvre d'alternatives et de solutions innovantes ont été faites pour les sous-secteurs industriels suivants : soit formulation de peinture, application de la peinture, finissage textile et polymères). Les évaluations des sous-secteurs dans chacun des pays participants ont mené à l'élaboration du présent ***manuel technique***, qui vise à susciter des idées novatrices produisant des solutions innovantes et rentables ainsi qu'à permettre aux entreprises de ces pays et aux sous-secteurs de mettre en œuvre une gestion écologiquement rationnelle des produits chimiques et des déchets chimiques à fort impact.

2 General description of Synthesis of Polymers

2.1 Main uses

2.1.1 Fields of application

Despite the central role plastics play in life today, there remains a trace of the old view that plastic products are cheap and nasty. Polymers, in the form of plastics, rubbers and fibres, have for many years played essential but varied role in everyday life. Polymeric materials are used in different end markets like building and construction, automotive, packaging, electric and electronic, etc. For these markets, there are different types and grades of plastics providing specific properties to meet the functional needs of applications. The top six types of plastics in terms of market share are: polyethylene – including low density (PE-LD), linear low density (PE-LLD) and high density (PE-HD), polypropylene (PP), polyvinyl chloride (PVC), polystyrene solid (PS), expandable (PS-E), polyethylene terephthalate (PET), and polyurethane (PUR).

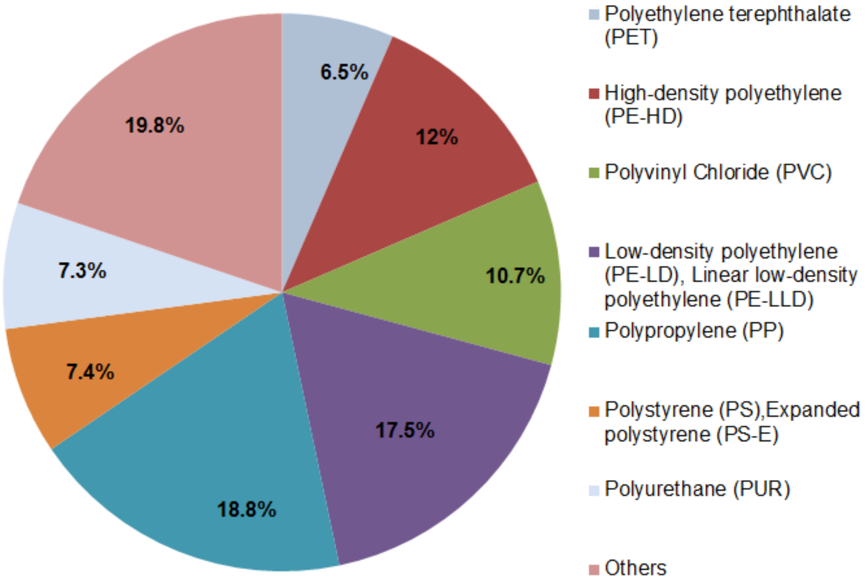


Figure 2-1: Main types of plastics in 2011 in EU [based on 23].

2.2 General processes and techniques applied in the production of polymers

The production of polymers follows the scheme given in Figure 2-2 with monomers, co-monomers, catalysts, solvents as well as energy and water on the input side and the product, off-gases, waste water and wastes on the output side.[3; p. 21]

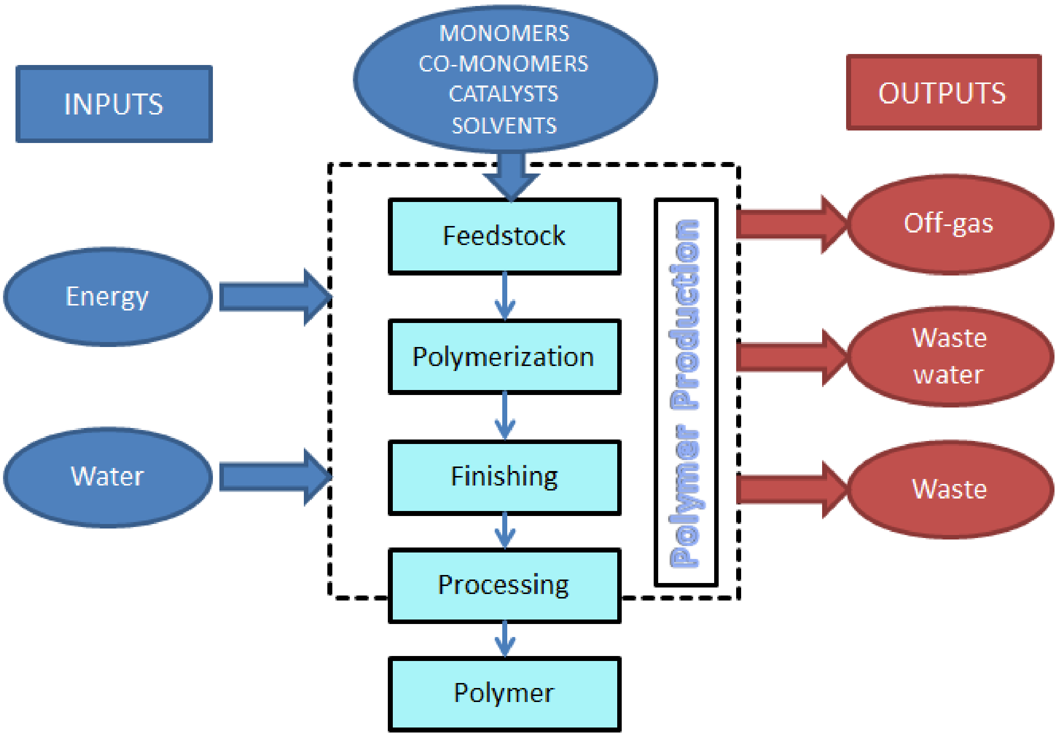


Figure 2-2 General production Scheme [3; p. 21]

The main feedstock used for the production of polymers are the monomers.

Important monomer groups are:

- ethylene, propylene, butadiene, isoprene, styrene
- vinyl chloride, vinyl esters, , chloroprene
- acrylic and methacrylic esters, -amides and -nitriles
- adipic acid, hexamethylene diamine, caprolactam
- terephthalic acid, ethylene glycol
- formaldehyde
- aromatics, like phenol, cresol, bisphenol A
- maleic anhydride.

Also general purification units like distillation, extraction or fractionated crystallisation are usually part of the monomer supply. [3; p. 21]

2.2.1 Polymerization (chain growth reaction)

Polymerization is the most important reaction process and produces amongst others the plastics polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). The reaction principle includes the opening of the double bond of a monomer and linking many monomeric molecules together forming a saturated long chain macromolecule. [3; p. 23]

Depending on the activation (type of reaction initiation), a differentiation is made between radical and ionic polymerization:

- radical initiators may be oxygen, or for higher process temperatures, organic peroxides or azocompounds or simply heat as in the case of polystyrene, and for lower processing temperatures redox systems such as persulphate/bisulphite

- ionic (including organo-metallic) catalysts are mostly of a very complex nature and often require a separate production process within the plant. Modern ionic catalysts are so effective that removal of the catalyst after polymerization is not required for most of the applications. Only one gram of transition metal, for instance, produces more than 200 tonnes of final products. Thus, the residual concentration of the transition metal is no more than a few parts per million [3; p. 23]

These reactions are usually exothermic, thus producing energy. The actual polymerization may be carried out in bulk, in water or in organic solvents or dispersants. [3; p. 24]

Probably the most general classification scheme is based on the polymerization mechanism involved in polymer synthesis. Under this scheme, polymerization processes are classified as step-reaction (condensation) or chain-reaction (addition) polymerization. In this chapter, we will discuss the different types of polymers based on the different polymerization mechanisms. The basic of chain-reaction polymerization mechanism are:

The course of the reaction process can be generally described as:

- start reaction (or initiation)
- growth reaction (or propagation)
- termination reaction.
- chain transfer
- diene polymerization

Polycondensation (step growth reaction)

Step-growth polymerization involves a series of reactions in which any two species (monomers, dimers, trimers, etc.) can react at any time, leading to a larger molecule. Most step-growth polymerizations, as we shall see presently, involve a classical condensation reaction such as esterification, ester interchange, or amidization. In step-growth polymerization, the stepwise reaction occurs between pairs of chemically reactive or functional groups on the reacting molecules. In most cases, step-growth polymerization is accompanied by the elimination of a small molecule such as water as a by-product. [20, p.47]

The reaction principle includes the reaction of a monomer with two distinctive reactive functional groups or the combining of two bi-functional monomers forming a polymer and generating a by-product which is in many cases, water. [3; p. 24]
The process often (but not always) needs a catalyst which is usually a metal salt or a combination of metal salts. [3; p. 25]

Polyaddition

The reaction principle includes the opening of a reactive ring, or a reactive group forming a polymer. The characteristic of these processes closely follows those of polycondensation reactions; thus, a stepwise growth can be observed. An advantage – also from an environmental point of view – is that there are no formation of low molecular weight products. [3; p. 26]

2.2.2 Polymer production processes

Polymerization processes may be conveniently classified as homogeneous or heterogeneous. In homogeneous polymerization, as the name suggests, all the reactants, including monomers, initiators, and solvents, are mutually soluble and compatible with the resulting polymer. On the other hand, in heterogeneous systems, the catalyst, the monomer, and the polymer product are mutually insoluble. Homogeneous polymerization comprises bulk (mass) or solution systems while heterogeneous polymerization reactions may be categorized as bulk, solution, suspension precipitation, emulsion, gas phase, and interfacial polymerization. [20, p.258]

Generally, the reaction of monomers to polymers may be carried out discontinuously or continuously by one of the following processes: [3; p. 26]

Suspension polymerisation

In suspension polymerization, the chemical reaction takes places in droplets that are in suspension in a solvent. Suspension polymerization is characterized by a good transfer of the reaction heat, a low dispersion viscosity and low separation costs on the one side but also by the fact that it is a discontinuous process, and there are relatively high amounts of waste water, significant reactor wall fouling and suspension agents remaining in the final product and in the waste streams. [3; p. 26-27]

Typical products made by suspension processes are:

- polyvinyl chloride
- polymethyl methacrylate
- polystyrene (HIPS and EPS)
- polytetrafluoroethylene
- polyolefins as slurry in mineral oil fractions.

Suspension polymerization has numerous attractive features. First, the economical use of water as the heat exchange medium is most common than the organic solvents. Secondly, the removal of the excessive heat of polymerization presents minimal problems, and control of temperature is relatively simple when water is used. Another advantage is the quality of the product obtained because separation and handling are relatively easier and so little amount of catalyst, suspension and dispersing agents remaining in the resins after the purification process.

Suspension polymerization is the most widely used process for making plastic resins both in terms of the number of polymer products and in tonnage production. Polymers such as styrene, methyl methacrylate, vinyl chloride, vinyl acetate, the fluorocarbons, and some gaseous monomers, including ethylene, propylene and formaldehyde, are polymerized by the suspension polymerization process. [20, p. 262]

Bulk polymerisation

Small amount of an initiator are present. Bulk polymerization processes are characterized by high product purity, high reactor performances and low separation costs, but also by high viscosities in the reactors. Bulk processes cause reactor fouling, and in the case of polycondensation products, a high vacuum is required. Bulk polymerization is widely used in step-growth polymers production process and is suitable to manufacture pure polymeric products, i.e. in the manufacture of optical grade poly (methyl methacrylate) or impact-resistant polystyrene, because of minimal contamination of the product. However, removal of the unreacted monomer is usually necessary, and this can be a difficult process. [20, p.258-260]

Typical products made by bulk processes are:

- polyolefins
- polystyrene
- polyvinyl chloride
- polymethyl methacrylate
- polyamides
- polyesters.

This method can be used for chain-growth polymerization, but only on a small scale, preferably at low temperature. Heat and bubble transfer may give problems, since the degree of polymerization (and hence, also the viscosity of the reaction mixture) increases very rapidly from the beginning of the reaction. [3; p. 27]

Emulsion polymerisation

In a solvent – like in the case of suspension polymerization – but also in emulsion structures called micelles, and in the solvent. Emulsion processes typically show a low dispersion viscosity, good heat transfer, high conversion rates and are suitable for the production of high molar mass polymers. They are also characterized by high separation costs, reactor wall fouling and emulsifiers remaining in the product and in the waste streams. [3; p. 28]
Emulsion polymerization is widely used commercially for the production of a large variety of polymers. All polymers made by this process are addition polymers rather than condensation polymers and require free-radical initiators. [20, p.267]

Typical products made by emulsion processes are:

- ABS
- polyvinyl chloride
- PTFE
- SBR
- NBR
- PVA
- PMMA
- polyacrylates for paints.

Gas phase polymerisation

In gas phase polymerization, the monomer is introduced in the gaseous phase and put in contact with a catalyst deposited on a solid structure. Gas phase processes allow an easy removal of the reaction heat, they are low in emissions and waste and no additional solvents are needed. Gas phase processes are not applicable for all end-products and the investment costs are relatively high, partially caused by the high pressure equipment needed for most of the processes. [3, p. 29]

Currently, gas phase processes are only applied to the polyolefins:

- polyethylene
- polypropylene.

Solution polymerization

In solution polymerization, the chemical reaction takes place in a solution of the monomer in a solvent. The advantages over bulk, emulsion, and suspension polymerization techniques are [Polymer science, p. 261], [3; p. 29]:

- high efficiency of polymerization (easy removal of catalyst-simplifies purification)
- less heat transfer problems by using an inert diluent solvent increasing overall heat capacity without contributing to heat generation and by conducting the polymerization at the reflux temperature of the reaction mass, the heat of polymerization can be conveniently and efficiently removed
- a low dispersion viscosity and little reactor wall fouling
- mixing is facilitated because the presence of the solvent reduces the rate of increase of reaction medium viscosity as the reaction progresses.

Solution polymerization, however, has a number of drawbacks [3; p. 29], [20, p. 261]:

- The solubility of polymers is generally limited and low and requires that vessels be larger for a given production capacity.
- The inert solvent lowers the yield per reactor volume and reduces the reaction rate and average chain length
- The solvent frequently presents hazards of toxicity, fire, explosion, corrosion, and odour problems not associated with the product itself.
- solvent handling and recovery and separation of the polymer involve additional costs, and removal of unreacted monomer can be difficult. Complete removal of the solvent is difficult in some cases.

Typical products made by solution processes are:

- polyacrylonitrile
- polyvinyl alcohol
- SBR
- BR
- EPDM
- polyethylene.

Solution polymerization is a limited commercial process but finds ready applications when the end use of the polymer requires a solution, as in certain adhesives and coating processes [i.e., poly(vinyl acetate) to be converted to poly(vinyl alcohol) and some acrylic ester finishes]. Solution polymerization is used widely in ionic and coordination polymerization too. [20, p. 262]

2.3 Main products

2.3.1 Polymers based on crude oil

Different market requirements have resulted in a wide range of polymeric materials which are grouped into: [3; p. 6-7]

Structural materials where the polymer is the main and most visible structural component with the subgroups:

- **Commodity polymers** (polyethylene, polypropylene, polystyrene, polyvinyl chloride, ESBR, etc.). Such polymers are used in large quantities at relatively low costs for major applications like tubes, films, profiles, containers, bottles, sheets, tyres, etc.
- **Engineering polymers and speciality rubbers** (ABS, polyamides, polyesters, polyacetals, polymethy methacrylates, EPDM, NBR, etc.). Such polymers are used for special requirements at an intermediate cost level often for very small parts (clips, valves, special machine parts, etc.)
- **High performance products** (polyimide, polytetrafluoroethylene, polysulfone, polyetherketone, fluorinated and silicone rubbers, etc.). Such low volume, high priced materials are used to meet extreme requirements like high temperature, weather or solvent resistance, special wear or optical properties, extreme purity for critical medical applications, etc.)
- **Thermosetting polymers** (polyesters, epoxies, phenolics and alkyd resins) often used as coating resins and binders for fibrous reinforcements in a range of applications from boats to brake linings.

Functional materials where polymers are used as an aid to achieve a special function. They mostly constitute a small and often invisible part of the total system only with the following subgroups:

- **Commodity applications** like dispersants, detergents, flocculants, thickeners, super absorbers or adhesives and glues. Here, large volume polymers based on polyvinyl acetate, polyacrylic acid and its derivatives, and polyvinyl alcohol are used
- **Special technical applications** like membranes, optical fibres, products with electrical conductivity, and light emitting products. Here, high priced materials are used in small amounts where the functionality, and not predominantly the mechanical properties, is important.

2.3.2 Polymers based on renewable resources

- fibres from cellulose (cotton) or derivatives (cellulose acetate)
- fibres from polypeptides (wool)
- plastics from cellulose acetate
- Rubber from tree resin (polyisoprene).

Generally, renewable raw materials can be used to produce either long-term living products like construction materials for automobiles, ships and for the building and construction sector, or short-term living products like compostable packaging or biodegradable mulch films. [3; p. 7]

2.3.3 Biodegradable polymers

Today, biodegradable products are developed for markets where biodegradability is considered a technical advantage like for instance: [3; p. 8]

- mulch film in agriculture
- garbage bags for composting which can provide easier handling and eco-efficient benefits for waste management
- paper coating
- hygiene films including funeral applications, sanitary towels.

3 Innovative solutions

Polymer production is a diverse field with many varying types of polymers and production and even with the same polymer type, having differing production processes (e.g. for polystyrene there are three main types of production processes). Therefore, this sub-sector manual will present an overview of:

- Generic Techniques (generally valid for all production techniques)
- Polystyrene techniques
- Unsaturated Polyester techniques

The innovative sections pertaining to the synthesis of polymers is structured as follows:

Reduction of chemicals

- Increased reagent conversion through improved reactor design
- Minimization of plant stops and start-ups & containment systems
- Equipment design to minimize VOC losses
- Fugitive loss assessment & measurement and Equipment monitoring and maintenance
- Pigging systems
- Minimization of flared streams from discontinuous sources
- feeding systems (solid conveyer and metering systems, liquid metering)
- improved reaction for higher conversion (e.g. Sulzer flow reactor)
- Example: PS, GPPS technique
- Example: UP techniques

Substitution of hazardous chemicals

- Example of PFTE recycling? Not hazardous chemicals

Reduction of chemical waste

- Re-use of waste
- Reduction of dust emissions
- Water pollution prevention

3.1 Reduction of chemicals consumption

3.1.1 Increased reagent conversion through improved reactor design

A higher conversion of raw materials to product can be achieved through the use of improved mixing, optimized reactor performance, and better temperature control.

One example of improved reactor design is that by Sulzer Chemtech; they have developed and introduced a new generation of reactors based on the principle of static mixing and on the continuous bulk polymerization, e.g. mass- and solution polymerization. This reactor is abbreviated as SMR (Sulzer Mixing Reactor) and is characterized by accurate control of heat transfer and mixing effects so that high conversion and consistently high polymer quality are achieved time after time in order to meet varied and stringent requirements.

The plug-flow nature of the reactor inherently results in increased conversion. The advantages of such advanced reactor systems include:

- reduced consumption of raw material (high conversion rate)
- prevention of large quantity of off-spec product during product grade switch
- fast self-cleaning and start-up procedure
- reduced energy requirements (minimum hydraulic pressure loss, lack of agitator)

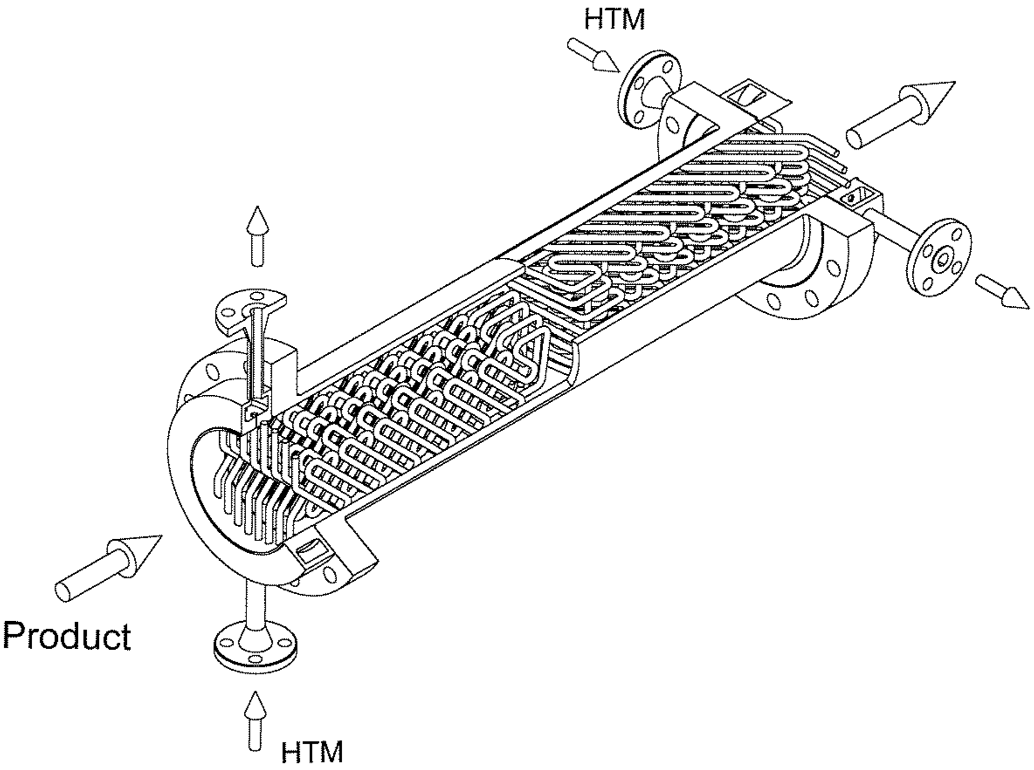


Figure 3-1 Cutaway of the SMR reactor (©Sulzer Chemtech Ltd) [4; p. 5]

3.1.2 Minimization of plant stops and start-ups and containment systems

Through improved operation stability (assisted by computer monitoring and control systems) and equipment reliability, the need for plant stops and start-ups is reduced to a minimum. Emergency stops can be avoided by timely identification of deviating conditions followed by the application of a controlled shut down process. Through the minimisation of shut downs, including emergency stops, and start-ups the emission of VOC as well as dust is reduced, thereby resulting in less chemical loss (products as well as raw materials). [3; p. 196]

Emissions occurring during plant start-ups, shut downs and emergency stops are sent to a containment system to avoid their emission to the environment. The contained material, which can be unreacted monomers, solvents, polymers, etc. are recycled if possible or used as fuel, e.g. in the case of polymers of undefined quality.

Through the containment of the emitted reactor content, emissions of dust and hydrocarbons to the environment are avoided. The contained material can (product, monomers, and solvents) be recycled back into the process and/or used as fuel. [3; p. 196-197]

Another measure to reduce plant stops and start-ups is to prevent polymer built-up at walls in reactors and other equipment using anti fouling agents.

Example: Noxol, Everplus [17]

AkszoNobel products - Noxol® and Everplus - are key ingredients in the manufacture of suspension PVC. They also find growing use in the production of styrenic and acrylic (co)polymers.

These antifouling agents prevent reactor fouling and polymer build-up, which are known to reduce heat transfer and product quality. In addition, they offer savings in operational costs and time by reducing cleaning time between batches.

Noxol provides better adhesion to the reactor wall, while its functional groups protect against negative interaction with oxygen. In addition, it is specific due to its colour and transparency, which makes it visual distinct from all products available in the market.

Example: Evicas 90CS [18]

This additive is used to prevent polymer build-up in reactors and condensers of all the different PVC homopolymer, copolymers and paste/ emulsion manufacturing processes. No adverse effect on PVC properties when applied evenly and without excess. It could be used for emulsion and copolymer as well as for suspension PVC or other free radical processes. It aids to prevent PVC build-up in troublesome areas e.g. agitator blades, agitator shaft, internal baffles and condenser tubes. Just a few kg (or less) needs to be applied during the manual clean. This specific additive allows prolonged operation of a reactor, usually for a closed process, before manual cleaning of the reactor is required. In addition, it reduces reactor downtime and allows increased PVC productivity per annum. And it maximises reactor heat transfer by minimizing the build-up of polymer.

3.1.3 Collect and reuse monomers from finishing and processing steps

Example: Collection and reuse of unreacted VCM in PVC Production [19]

Polyvinyl chloride (PVC) is produced by polymerization of vinyl chloride monomer (VCM). Unreacted VCM is pumped out of the reactor and condensed, and non-condensable gases are vented from the condenser. Depending on the temperature and pressure of the condenser, the vent stream also contains from 50 to 2,000 lb/h of VCM. As VCM emissions are tightly regulated, the vent stream must typically be incinerated and scrubbed before release.

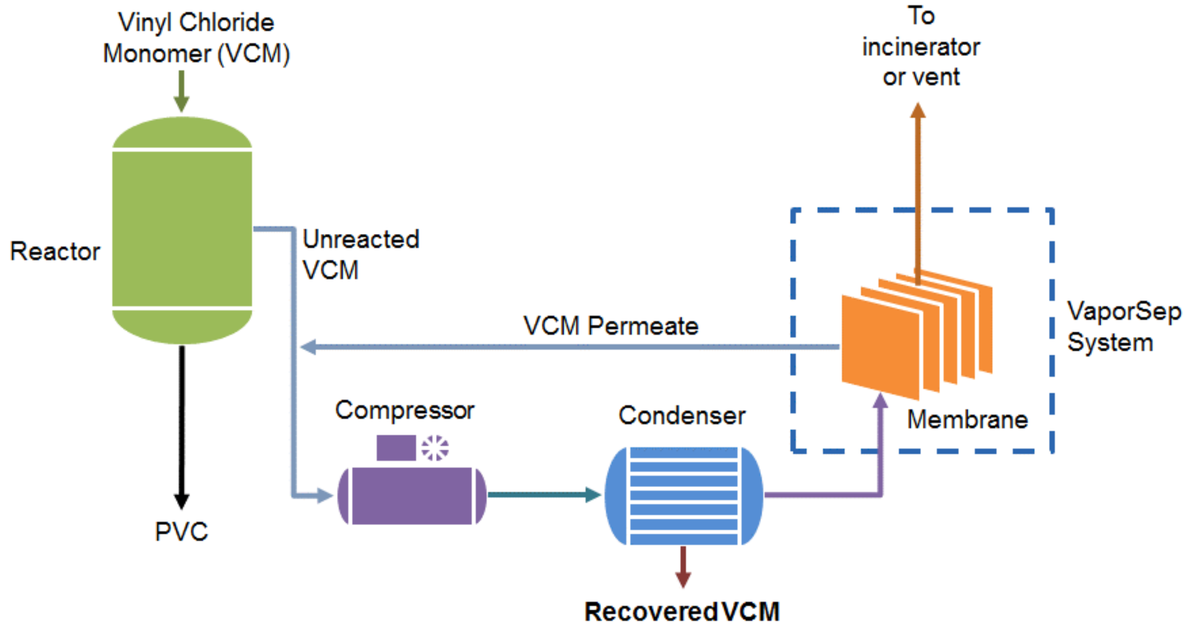


Figure 3-2 VaporSep® Solution process [based on 19]

The vent stream from the existing VCM condenser is sent to the VaporSep system (see Figure 3-2). VCM passes through the membrane at a greater rate than inert gases, producing a VCM-enriched permeate and a VCM-depleted residue. The permeate is recycled to the inlet of the existing compressor and the residue is incinerated. The VCM recovered by the VaporSep system is condensed in the existing condenser.

VaporSep systems allow PVC producers to recover 90% to 99+% of the VCM currently lost in vent streams, providing a significant economic benefit.
VaporSep systems are currently used by major PVC producers including Oxyvinyls, Westlake, Solvay, and Aiscondel.

Benefits

- Achieves significantly higher VCM recovery than possible by condensation alone
- Achieves recovery at more moderate temperatures and pressures than condensation alone
- Minimizes footprint and weight
- Minimizes maintenance with no moving parts
- VCM recovery up to 99+%

System Description

- Complete, skid-mounted unit includes all necessary instrumentation and controls
- Unit dimensions: 6 to 15 ft. (L) x 6 ft. (W) x 6 ft. (H); 5,000 to 15,000 lb

System Performance

- Suitable for vent streams from 50 lb/h to greater than 2,000 lb/h, with VCM concentrations from 20 to 80 vol%

3.1.4 Reduce fugitive emissions

Reduce fugitive emissions through technical provisions

Technical provisions to prevent and minimise fugitive emissions of air pollutants include: [3; p. 192]

- Use of valves with bellow or double packing seals or equally efficient equipment. Bellow valves are especially recommended for highly toxic services
- Magnetically driven or canned pumps, or pumps with double seals and a liquid barrier
- Magnetically driven or canned compressors, or compressors using double seals and a liquid barrier
- Magnetically driven or canned agitators, or agitators with double seals and a liquid barrier
- Minimisation of the number of flanges (connectors)
- Effective gaskets
- closed sampling systems
- Drainage of contaminated effluents in closed systems
- Collection of vents.

Reduce fugitive emissions through loss assessment and measurement and equipment monitoring and maintenance

A good fugitive loss measurement and repair programme requires an accurate calculation of components and the establishment of a database. In the database, components are classified in terms of type, service and process conditions to identify those elements with the highest potential for fugitive losses and to facilitate the application of industry standard leak factors.

Accurate results can also be obtained when specific correlations are applied which have been developed from a set of comparable plants.

Further information can be found in the LVOC BREF Section 5.3.1.3. [5; p. 106-108]

Likewise, the established component and service database provides the basis for a routine monitoring and maintenance (M&M) programme or leak detection and repair (LDAR) programme. Components leak rates are checked on a regular basis using an organic vapour analyser. Leaking components are identified for repair and future monitoring. Over time, it is possible to build up a picture of priority areas and persistent critical components enabling effective targeting of maintenance work and/or improvement in design.

Further information can be found in the LVOC BREF Section 5.3.1.3. [5; p. 108-112] and in the MON BREF. [6]

An optimised maintenance and repair programme of the installation leads to a reduction in VOC emissions and lost chemicals. [3; p. 193-194]

3.1.5 Pigging Systems

Pigging technology is a subdivision of materials transport and cleaning technology. In pigging, the contents of a pipe are pushed by a close fitting plug (pig), to push the product almost completely out of the pipe. The pig is most frequently driven by a gaseous propellant (e.g. compressed air). The main components of an industrial pigging system are:

- pig
- piggable pipe with piggable valves
- pig loading and unloading station
- propellant supply
- Control system.

Pigging can be applied in various locations, e.g.:

- between vessels in a production plant
- process plant – tank farm
- tank farm – filling facilities

The main achieved environmental benefits include:

- no rinsing procedures or substantially smaller amounts of cleaning agents required
- lower load in rinsing waters
- reduced loss of valuable product.

Pigging is especially attractive for long pipelines, multi-product plants, and batch operations. [3; p. 206]

3.1.6 Minimization of flared streams from discontinuous sources

A major potential source of discontinuous emissions in the polymer production processes is the reactor system. Discontinuous emissions from reactor systems occur during plant start-ups (for instance purging), shut downs and emergency stops.

Flare systems are used to treat discontinuous emissions. For flare systems, high efficiency burning tips and the injection of steam to suppress smoke formation are used to minimise emissions. Potential flows sent to the flare for incineration might include:

- gaseous hydrocarbon purge flows during start-ups and shut downs

- ethylene purge flows to control the build-up of inerts in the process
- hydrocarbon vapours from the intermediate purge section.

Hydrocarbon flows to be sent to a flare system are minimised by the following means:

- gaseous hydrocarbon purge flows during start-ups and shut downs:
    - reduction of the need for hydrocarbon purge by using nitrogen to make the unit free of O2 before start up
- ethylene purge flows used to control build-up of inerts in the process:
    - recycling to a light hydrocarbon complex for reprocessing
    - use of purge ethylene as fuel
    - installation of a separate distilling purification unit to remove inerts and higher hydrocarbons.

The last technique will not completely avoid flaring, but will reduce it:

- hydrocarbon vapours from the intermediate product purge section:
    - hydrocarbon purge can be greatly reduced through the application of a closed loop nitrogen purging/condensing system.

Further information can be found in the CWW BREF Section 4.3.2. [7; p. 295-305]

3.1.7 Utilisation or recovery of VOC emissions

Overview of Volatile Organic Compounds (VOCs)

VOCs are of serious environmental concern because of the harmful or offensive properties that they exhibit in varying degrees. These include:

- Harmful effects on human health & on natural ecosystems through toxicity, carcinogenicity and other adverse physiological effects.
- Damage to materials.
- Contribution to photochemical ozone creation at ground level with consequent harmful effects.
- Destruction of stratospheric ozone.
- Contribution to global climate change
- Sensory effects such as malodour.

Petrochemical production processes are rather specific to the feedstock and product and so are the process emission sources and the air pollutants. However the petrochemical processes utilise many common activities and thus it is possible to consider in a generic manner where the air emission streams may arise and what those streams may contain. Broadly petrochemical production unit producing a specific intermediates or final product generally involves distinct processing modules viz.:

- Feed raw material supply and pre-treatment
- Synthetics
- Production separation, refinement and co-product recovery

Besides the specific unit may involve intermediates product storage and handling and also dedicated disposal system for gaseous streams like incinerators etc. The emission sources from the petrochemical complex are classified also as “point sources” and “non-point sources” as given below:

Point sources

- Combustion sources (power and steam generation)

- Process / intermittent vents
- Emission due to transfer process
- Storage emission
- Emission control and disposal modules (Viz. flare, incinerator etc.)

Non Point sources (Fugitive emission)

- Equipment leak
- Cooling water, wastewater collection and treatment system

Table 3-1 VOC Emissions in Petrochemicals/ SOCMI/ Polymer Process [based on 21, p.117 – 122]

Name of chemical / product	Type of Emissions	Pollutants expected
Ethylene / Propylene	• Oxides of Carbon & Nitrogen from incineration of waste gases, generation heaters & acetylene generation reactor • HC's during shut down & start-up • Fugitive releases particulates & combustion products from decoking operations	Ethylene, Propylene, Acetylene, CO & NOx
Butadiene	Hydrocarbons from reactor & storage tank vents & during process plant decommissioning for maintenance	Butylene, Butadiene
Benzene / Toluene /Xylene	• Charge gas & Refrigerator compressors are potential sources of Hydrocarbons • Furnace decoking, Acid gas removal & catalyst re-generation (do not have hydrocarbon emissions) • Fugitive emissions from Pumps, Valves, Compressors, Storage Tanks	Benzene, Toluene, o-, m- & p- Xylene
Methanol	• Purge gas containing CO / CO_2/ CH_3OH & other hydrocarbons • Fugitive emission from pumps, valves, compressors, storages etc.	CO/CO_2/ Methanol
PVC	• VCM from reactors, monomer recovery & PVC stripping & drying • PVC particulate matter from transfer & storage • VCM from waste water collection & treatment	Vinyl chloride
PE	• Purges of feed stocks or solvents or the products or their combustion • HC from raw material storage, degasser hoppers • Fugitive losses of feed stock & solvent HC • Vents from catalyst preparation systems possibly with organometals • Vents at high pressure (LDPE)	Ethylene
Poly Styrene	• Propylene particulate matter from vents (on dust extraction, extruder, extruder extract) • Propylene / propane from powder vessel vent • VOC's from extruded extract vent • Polymer dust from granulate transport air	Propylene
Vinyl Acetate Monomer	• HC's from reactor loop purge • CO_2 Purge vent from absorption/desorption system	Acetaldehyde, Ethylene, Acetic acid
Cyclohexane	Fugitive emission from pumps, valves, compressors & storages. Vent releases during shutdown	Benzene
PP	• Propylene particulate matter from vents (on dust extraction, extruder, extruder extract) • Propylene / propane from powder vessel vent • VOC's from extruded extract vent • Polymer dust from granulate transport air	Propylene
Ethylene Oxide	• CO/CO_2 & HC from loop purges & CO_2 absorber vent • EO from the reactor analysis vent purification process and storage vent • Small amounts of EDC, used in small quantities to modify the oxidation reaction, are also released	Ethylene oxide/ CO/CO_2/ethylene/ Ethylene Glycol

3.1.8 Examples of BAT specific to Polystyrene production (GPPS method)

Below is given an example of BAT for chemicals consumption and waste produced:

Table 3-2 BAT for chemicals consumption and waste produced in PS production [based on 3; p. 263]

GPPS	Unit per tonne product	BAT AEL
Air emissions		
Dust	*g*	20
VOC, total	*g*	85
Water emissions		
COD	*g*	30
Suspended solid	*g*	10
Hydrocarbons total	*g*	1.5
Waste water	*t*	0.8
Cooling tower purge water	*t*	0.5
Waste		
Hazardous	*kg*	0.5
Non-hazardous	*kg*	2
Consumptions		
Total energy	*GJ*	1.08
Styrene	*t*	0.985
Mineral oil	*t*	0.02
Cooling water (closed circuit)	*t*	50
Process water	*t*	0.596
Nitrogen	*t*	0.022
Diluent	*t*	0.001
Additives	*t*	0.005

1. *The emission values in the water are measured after treatment. The waste water treatment facility can be inside the plant or at a centralised location*
2. *Not including cooling water purge water*
3. *Hazardous waste (to treatment or incineration) in kilograms per tonne of product (kg/t)*
4. *Inert waste (to landfill) in kilograms per tonne of product (kg/t)*

The following table presents various techniques available for reducing emissions generated during the GPPS process for the producing polystyrene:

Table 3-3 Techniques for emissions reduction during polystyrene production [based on 3; p. 222]

Emissions	Available techniques	Cost	Efficiency	Remarks
Gaseous				
Storage	Minimise level variation Gas balance lines Floating roofs Condensers installed Vent recovery to treatment	L M H H H	M M H H H	Only for integrated sites For adjacent tanks For large tanks only
Process equipment	Collect vent	H	H	
Dust	Pelletiser Filters Hydrocyclones	H H H	M M M	Type and size dependent
Pelletiser	Collect and treat	H	M	
Liquid				
Purge	Recovered to be used with fuel oil or incinerated	M	H	
Waste water	Biological treatment*	L	H	
Solid waste**				
Hazardous and non-hazardous waste	Minimise the volume by good segregation Collect to external treatment	L M	M H	
Management techniques		M	H	

* existing treatment plant

** only insignificant quantities

Note: *L: low, M: medium, H: high*

3.1.9 Examples of BAT specific to Unsaturated Polyester production

The following table displays the emissions and consumption levels associated with BAT in the production of unsaturated polyester.

Table 3-4 Emissions and consumption levels in the production of unsaturated polyester [based on 3; p. 269]

Unsaturated Polyester	Unit	BAT AEL range	
Consumptions			
Energy	GJ/t	2	3.5
Water	m^3/t	1	5
Emissions to air			
VOC to air	g/t	40	100
CO to air			50
CO_2 to air	kg/t	50	150
NO_X to air	g/t	60	150
SO_2 to air	g/t	~0	100
Particles to air	g/t	5	30
Waste			
Hazardous waste for external treatment	kg/t		7

Treatment and recovery of solvent from waste gas [3; p. 234]

Waste gas streams are generated from several sources (in particular process vessels), which have to be treated prior to emitting the remaining gas to the air. The most widely used technique to treat these gases is thermal oxidation.

However, other technologies are available and used as well. An example is activated carbon adsorption used for VOC removal from vent streams that are relatively low in flow and VOC concentration.

Other examples are:

- glycol scrubbers used to treat vent streams from maleic and phthalic anhydride storage vessels
- sublimation boxes (cold traps, allowing sublimation of anhydrides, including a system of maintenance, cleaning and rework of recovered material).

Thermal oxidation

Two types of thermal oxidiser are in common use: regenerative and recuperative oxidisers.
Regenerative oxidation tends to be the more efficient of the two as it uses the recovered energy to pre-heat incoming process air to oxidation temperatures (~800°C). Consequently, its operating costs are significantly lower than for recuperative oxidation systems. Regenerative thermal oxidation systems are widely used as they are relatively insensitive to the composition of the solvents in the process air and the concentration.
Recuperative systems are useful if the heat of the exhaust gas can be used in different areas of the plant. Steam or thermo-oil is heated via heat exchangers. They are mainly used for small flow rates. At higher rates the systems are not cost effective. They are often used in combination with catalytic oxidation systems.
Thermal oxidation systems are used for inlet concentrations between 1 - 20 g/Nm^3. VOC destruction efficiency rates of up to 99.9 % are possible. The minimum VOC concentration for the oxidation process to be autothermic is 1 - 2 g VOC/Nm^3. [8; p. 365]

Active carbon

Active carbon physically adsorbs the VOC to separate it from the gas stream. After the sorbent bed is saturated the VOC it is desorbed as a concentrated vapour using hot gas or steam. The concentrated VOC may then be recovered by condensing as a liquid. (The desorbed VOC may also be oxidized; because it is in a concentrated form. Energy recovery is not an issue). [9; p. 1]

Sublimation boxes

A refrigerated condenser works best with emission streams containing high concentrations of VOC. The air stream is cooled below the dew point of the solvent. Then the solvent condenses and it can be reused. The exhausted air stream leaving the condenser will still contain some solvent. In a closed loop system, the overall solvent emissions are greatly reduced. If the system uses air, care has to be taken, that the solvent concentration in the air is less than 5 % of the lower explosion limit (LEL). While using inert gases (i.e. N2) concentrations up to 50% LEL can be used, and this option reduces the drying time and the length of the drier. A disadvantage of using inert gases is the required flushing and refilling of the system with inert gas after each equipment down time or outage. [8 ; p. 366]

Glycol scrubbers

Absorption, or scrubbing, is often used to separate gaseous streams containing high concentrations of organics, especially water-soluble compounds such as methanol, ethanol, isopropanol, butanol, acetone and formaldehyde. It is widely used to abate VOC/HAP emissions during natural gas purification and coke by product recovery. However, it is more commonly used for controlling inorganic gases, such as HCl, than for VOCs/HAPs. [10; p. 32]

3.2 Substitution of hazardous chemicals

3.2.1 Using Safer Chemicals

Modified Silane Polymers [11]

Modified silanes are one component adhesives which react and cure under the action of moisture, during its curing process by polycondensation this type of adhesives emit methanol and once cured acquire elastic properties and typical strength of an elastomeric material.

Modified silanes are used in all those applications that are used for polyurethane elastic adhesives, due to various advantages presented by these adhesives, industries are increasingly incorporating modified silanes in its processes.

Polyether modified silanes are less resistant and more elastic compare with polyurethane modified silanes, latter are also known as hybrid polyurethanes.

One of the main advantages of the modified silanes do not require use of primers or adhesion promoters prior to adhesive application, in many cases cleaning of the surface is enough to ensure adhesion between the substrates, thereby reducing both cost of materials and cost of application, also avoid errors during the treatment surface before apply the adhesive. Modified silanes not cure under the action of polyols (short-chain polymers with OH groups), for that reason it is necessary to verify that the cleaner used to prepare the surface does not contain polyols.

The modified silane may be cured at a range of humidity between 30% and 95%, due that unlike polyurethanes do not emit CO_2 or any volatile compound which could cause internal bubbles in the adhesive reducing the mechanical and cohesive properties of the adhesive.

Chemical properties:

- Very good resistance to ultraviolet.
- They can be painted, even shortly be applied (wet on wet).
- Adhere to a wide range of materials (metal, ceramic and plastic) without primers or activators.
- Not contain isocyanates, improving health job.

Polycarbonate Production from CO_2 instead of CO and Cl [12]

The non-phosgene process for polycarbonate (PC) production developed by Asahi Kasei is the world's first to use carbon dioxide as a starting material. PC is conventionally produced using the hazardous carbon monoxide, phosgene, and methylene chloride as process materials. The new process not only eliminates the hazards associated with the use of these materials, but also features high productivity and yield, extremely little by-product, less contaminated process water requiring treatment, and low impurities in product PC. High-purity ethylene glycol (EG) is a co-product of the process.

Furthermore, more than about 90% of PC has been produced by the so-called “phosgene process,” and the PC contains Cl impurities. It needed to use not only highly toxic and corrosive phosgene made from CO and Cl_2 as a monomer, but also very large amounts of CH_2Cl_2 and water, and needed to clean a large amount of wastewater. The new process not only overcomes drawbacks in the conventional processes, but also achieves resource and energy conservation. The reduction of CO_2 emissions (0.173 tCO^2e per ton PC) is also achieved in the new process, because all CO_2 is utilized as the component consisting of main chains of the products.

The fields of applications include:

- Electrical and electronic equipment
- Automotive parts and accessories
- Medical devices
- Glazing for buildings
- Optical media

3.2.2 Biopolymers

Bio-based polymers produced from corn or sugarcane [24]

Bio-based polymers are defined as materials for which at least a portion of the polymer consists of material produced from renewable raw materials. For example, bio-based polymers may be produced from corn or sugarcane. The remaining portion of the polymers may be from fossil fuel-based carbon. Bio-based polymers generally have a lower CO_2 footprint and are associated with the concept of sustainability. Because of concerns about the depletion of fossil resources and the global warming associated with the use of petrochemicals, new bio-based polymers continue to be developed.

Several new bio-based polymers have been commercialized. A bio-based polycarbonate, isosorbide polycarbonate, can potentially be used as an alternative to petroleum-based polycarbonate. Corn-based isosorbide is used as a replacement for bisphenol A (BPA) monomer. Bio-based polybutylene succinate (PBS) resin prepared from bio-based succinic acid and bio-based 1,4-butanediol (BDO) can replace biodegradable petrochemical-based PBS. Green polyethylene has been commercialized with bio-based ethylene.

In the report “265 A Bio-Based Polymers” published by IHS Chemical in 2013 recent developments in bio-based polymers are discussed. This report reviews the production of the bio-based monomers required to produce isosorbide polycarbonate, polybutylene succinate, and polyethylene. The process economics for producing the monomers and polymers are evaluated. Comparative process economics for the conventional petroleum-derived polymers are included. This report will be of value to those companies engaged in the production of bio-based polymers and the conventional petroleum-derived-feedstock-based polymers.

PLA (Polylactic Acid) – a sustainable polymer

Polylactic acid or Polylactide (PLA) is a biodegradable, aliphatic polyester based on renewable resources. It is not an acid but in fact is thermoplastic aliphatic polyester derived from renewable resources, such as corn starch or sugarcane. PLA is commercially interesting because of its good strength properties, film transparency, biodegradability, and availability.

PLA has a wide range of applications including packaging, high heat packaging, fibres, consumer goods, and automotive.

Each type of bioplastic stemming from PLA has its own lifecycle, with differing consequences and different end-of-life options:

- Recycle & reuse (downcycling or upcycling)
- Renewable energy recovery (incineration)
- Compost/biodegrade
- Anaerobic digestion
- Feedstock recovery

Numerous market and strategy studies have shown that bio-based polyesters such as PLA have a bright future. The market for PLA has been steadily growing for years and will soon be increasing by millions of tonnes a year. Unlike standard plastics, the use of PLA conserves fossil resources, such as petroleum, while cutting greenhouse CO_2 emissions at the same time. The plastic also stands out for its biodegradability and very good recycling properties. The polymer-specific properties, such as its aroma and gas barrier, transparency and shine or twist effect, can be used functionally in a wide range of applications [13].

Example - Polylactic acid (PLA) technology, PLA*neo*® [25]

The engineering company Uhde Inventa-Fischer announced (December 2011) that they have proven the potential of its self-developed, patented polylactic acid (PLA) technology, PLA*neo*®. The process enables tailored PLA types for a full range of applications to be manufactured as well as enabling the production of different PLA specialties. During the test operation the full functionality of the PLA*neo*® process was proven and the desired performance parameters were also achieved. The completely continuous process is perfectly suited to large-capacity industrial production plants.

The feedstock for Uhde Inventa-Fischer's PLA process is lactic acid. The source of lactic acid is any raw material containing starch or sugar, such as corn, cereals, cassava, sugar cane or sugar beet. Lactic acid is expected to be sourced from non-food, cellulose materials within the next few decades.

Polyol Production [14]

Polyols are key ingredients in flexible polyurethane foams, which are used in furniture and bedding. Historically, polyurethane has been made from petrochemical polyols. The idea of replacing these polyols with bio-based polyols is not new, but the poor performance, colour, quality, consistency, and odour of previous bio-based polyols restricted them to limited markets. Previous bio-based polyols also suffer from poor chemical reactivity, resulting in foam with inferior properties.

Winners of the 2007 President's Green Chemistry Award, Cargill has successfully developed bio-based polyols for several polyurethane applications, including flexible foams, which are the most technically challenging. Cargill makes BiOHTM polyols by converting the carbon–carbon double bonds in unsaturated vegetable oils to epoxide derivatives and then further converting these derivatives to polyols using mild temperature and ambient pressure. BiOHTM polyols provide excellent reactivity and high levels of incorporation leading to high-performing polyurethane foams. These foams set a new standard for consistent quality with low odour and colour. Foams containing BiOHTM polyols retain their white colour longer without ultraviolet stabilizers. They also are superior to foams containing only petroleum-based polyols in standard tests. In large slabstock foams, such as those used in furniture and bedding, BiOH 5000 polyol provides a wide processing window, improved comfort factor, and reduced variations in density and load-bearing capacity. In moulded foams such as automotive seating and headrests, BiOH 2100 polyol can enhance load-bearing or hardness properties relative to conventional polyols.

Use of BiOHTM polyols reduces the environmental footprint relative to today's conventional polyols for polyurethane production. BiOHTM polyols "harvest" carbon that plants remove from the air during photosynthesis. All of the carbon in BiOHTM polyols is recently fixed. In conventional polyols, the carbon is petroleum-based. Replacing petroleum-based polyols with BiOHTM polyols cuts total energy use by 23 percent including a 61 percent reduction in non-renewable energy use, leading to a 36 percent reduction in carbon dioxide emissions. For each million pounds of BiOHTM polyol used in place of petroleum-based polyols, about 700,000 pounds (2,200 barrels) of crude oil are saved, thereby reducing the dependence on petroleum. BiOHTM polyols diversify the industry's supply options and help mitigate the effects of uncertainty and volatility of petroleum supply and pricing.

3.3 Reduction of chemical waste

3.3.1 Re-use of waste

Appropriate process-integrated measures help to prevent or reduce the amount of waste from a polymer plant, which contains waste solvent, waste oil, polymer waxes and scrap, purification bed agents and catalyst residues.
Waste solvent and oils can be used, where applicable, as cracker feedstock or as fuel. In some cases, concentrated polymer waxes can be sold as a by-product to the wax industry. Polymer scrap can be recycled. The usage of purification agents should be minimised through online regeneration and extended lifetime. Typically with the new generation of catalysts the efficiency is sufficiently high that catalyst residues can remain in the polymer, thus avoiding a catalyst wash step and the need to dispose of catalyst residues.
[3; p. 205]

3.3.2 Chemical Recycling to Produce Monomers

PLA Recovery and Chemical Recycling [15]

Currently, there are several options available on the market: incineration, composting, anaerobic digestion, land filling, etc. All these ends of life are not ideal because the plastic is not recycled back into its basic element (or monomer) and so it is not directly and perpetually reusable.

With the original LOOPLA® concept, GALACTIC is proud to contribute to the development of a more sustainable solution for the end-of-life management of PLA. LOOPLA® consists of a closed loop where the PLA wastes are recovered in order to recycle them into its monomer: the lactic acid. This one can be easily polymerized in order to recreate a new PLA with the same characteristics as the original one.

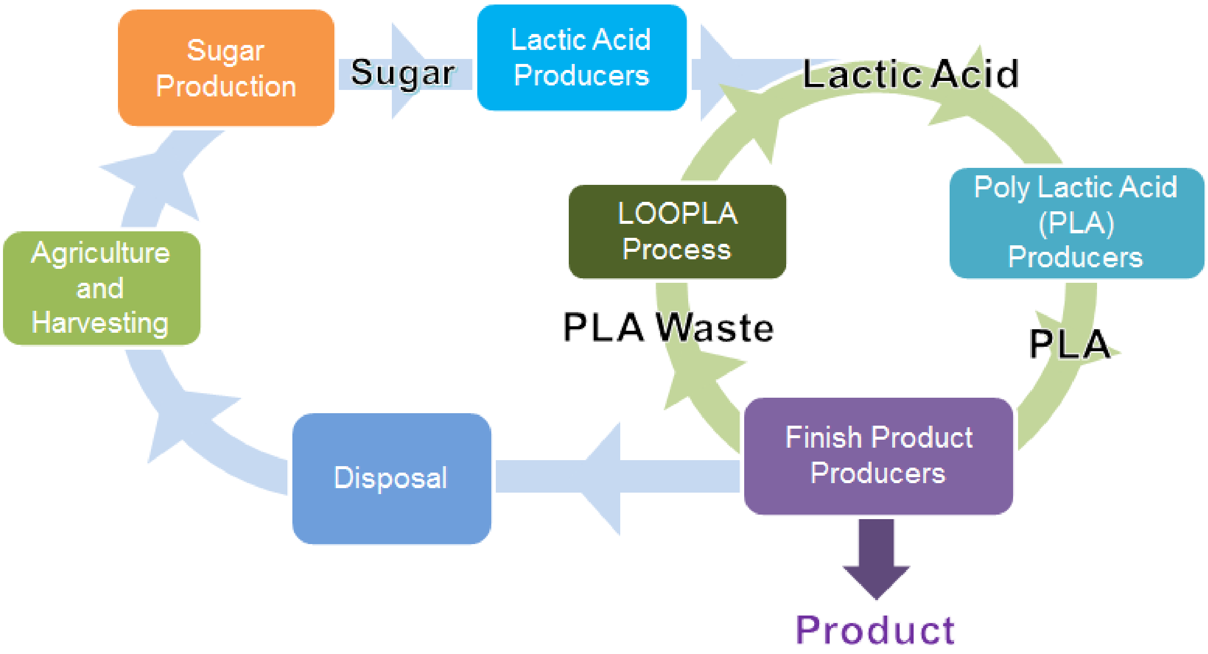


Figure 3-3 LOOPLA process description [based on 15]

LOOPLA® provides the best end-of-life option for PLA wastes, even though the PLA stream is contaminated. Unlike other treatments (incineration, anaerobic digestion, composting), it offers the possibility of directly going back to the original monomer by chemical recycling. In comparison with the other end-of-life management, the LOOPLA® is much more sustainable. Indeed this concept has a much higher positive impact on the environment. The carbon foot print is, therefore, much lower.

Re-use of PVC waste

Vinyloop® is a physical, solvent-based technology that is able to recycle difficult-to-treat, end-of-life PVC waste, and produces high-quality R-PVC (recycled PVC) compounds [26]. A centrifuge decanter (Figure 3-4 below) characterises the VinyLoop® unique process. This process separates the PVC compound from other materials (other plastics, rubber, metal, textile and others) by selective dissolution and filtration. It precipitates it into micro granules of PVC compound. The Vinyloop® process is using a solvent which runs in a closed loop. The regenerated PVC compound can be processed by extrusion, injection or calendering. The process improves the efficiency of the treatment of scraps containing fibres, and achieves a significant increase in tarpaulin recycling.

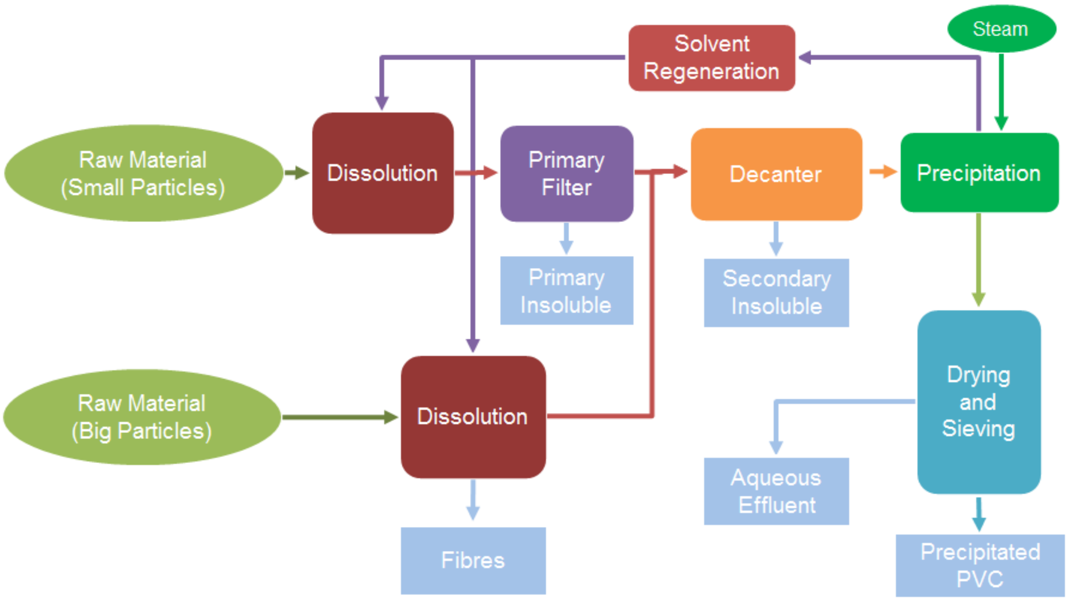


Figure 3-4 Process description Vinyloop® process [based on 26].

3.3.3 Reduction of dust emissions

The following techniques and good operating practices to reduce dust emission are to be considered in the determination of BAT: [3; p. 195]

- dense conveying is more efficient to prevent dust emissions than dilute phase conveying, although upgrading to the dense phase conveying is not always possible due to design pressure constraints
- reduction of velocities in dilute phase conveying systems to as low as possible
- reduction of dust generation in conveying lines through surface treatment and proper alignment of pipes
- Use of cyclones and/or filters in the air exhausts of dedusting units. The use of fabric filter systems is more effective, especially for fine dust
- use of wet scrubbers

3.3.4 Thermal treatment of wastewater

Various techniques exist to treat waste water: biotreatment, denitrification, dephosphatation, sedimentation, flotation, etc. Depending on the waste water effluent and its composition, and the plant operation, the most appropriate techniques are selected to treat the waste water.
The main part of the WWTP is usually the aerobic biological activated sludge process. Around this central facility a complex of preparatory and subsequent separation operations is grouped.
The facility may be a dedicated plant on the site of the polymer installation, a central facility in the site containing the polymer installation, or an external urban WWTP connected by dedicated pipeline or a sewer with little risk of storm overflow prior to the WWTP. The central waste water plant is normally equipped with:

- buffer or equalisation volumes, if not already provided by other upstream facilities
- mixing station, where neutralisation and flocculation chemicals are added and mixed (usually lime milk and/or mineral acids, ferrous sulphate); enclosed or covered if necessary to prevent releases of odorous substances, the captured exhaust air ducted to an abatement system

- primary clarifier, where the floc is removed; enclosed or covered if necessary to prevent fugitive releases of odorous substances, the captured exhaust air ducted to an abatement system
- activated sludge part, e.g.
    - aeration basin with nutrient feed at the entry, enclosed or covered if necessary with exhaust air ducts to an abatement system
    - or closed reaction tank (e.g. tower biology) with gas duct, connected to a gas abatement system
    - nitri/denitrification stage (optionally) and phosphate elimination
- optional intermediate clarifier, when a second aerobic biological stage is operated, with sludge recycling. [3; p. 208-209]

Waste water treatment in the production of polyester

Waste water in the production of polyester is mainly reaction water. This water is treated either on site or externally.

On site, this is treated by thermal oxidation. Combined equipment for the burning of liquid waste and waste gas, is currently the most general technique. The incinerators are also used for heat recovery. The incinerator may recover energy through steam or hot oil generation, which is used for process heating purposes.

An external method for the treatment of reaction water is leading or transporting it to a biological waste water treatment plant (WWTP).

An external method for the treatment of reaction water is leading or transporting it to a biological waste water treatment plant (WWTP) or in an anaerobic digester.

Achieved environmental benefits:

- destruction of VOC and COD/TOC in general from reaction water
- destruction of harmful organic compounds without burning of water
- no use of fuels
- no emissions to the air.

The applicability depends on the composition of reaction water; the biodegradability has to be tested. The biological options is less expensive than burning of water (depends on the transportation distance). [3; p. 235-236]

4 Cross-cutting innovative approaches

This section contains an introduction to cross-cutting innovative approaches for the sound management of chemicals and chemical waste that are valid for all sectors in the chemical product's value chain and not only in the sector which is the focus of this document.

The cross-cutting approaches and technologies include:

- How to use chemical leasing and other innovative business models to improve resource efficiency and safety in the value chain while also increasing competitiveness and enabling differentiation in a competitive market place
- How to understand the basic elements of a safety management system in order to reduce the risk of major accidents in facilities manufacturing or handling chemicals
- How to understand and use the Globally Harmonized System of Classification and Labelling of Chemicals to handle chemicals safely and responsibly
- How to safely store chemicals according to their hazard categories and minimize the risk of accidents
- How to develop a fire protection system, classify chemicals and implement technical risk reduction measures
- How to classify and manage hazardous waste effectively and remain in compliance with relevant regulations
- How to improve energy efficiency at facilities manufacturing or handling chemicals

4.1 Chemical leasing and other innovative business models

Chemical businesses are dependent on innovation and a continuous pipeline of innovative products and applications. This chapter provides an overview of known and successful chemical management business models.

4.1.1 Introduction to innovative business models

Greater spread and application of innovation in business models that reduce resource use has the potential to create multi-billion euro markets in the EU and overseas and achieve very substantial environmental and economic benefits. The actual spread of innovative business models currently covers a very broad range of sectors including industrial production of solid goods, fluids and ingredients as well as transportation, construction and maintenance, agriculture and public services. [27, p. 1]

4.1.2 Innovative chemical management business models

The chemical industry and the many companies that use its products have developed over time a linear business model in which raw materials are used to create valuable substances which are then, in turn, used to produce other products further down the value chain(s). Traditionally, chemicals are sold to customers, who become owners of substances and therefore responsible for their use and disposal. Their suppliers have a clear economic interest in increasing the amount of chemicals sold, which is usually related to negative releases to the environment. However, this is in opposition to the drive for resource efficiency and sustainability where the aim is to minimize resource use whilst maximizing added value.

Innovative service-based business models have the potential to resolve this problem. They aim to optimize the use of chemicals, save energy and encourage the recovery and recycling of chemicals. They also represent a better use of technical expertise and create an alignment of aims and business models and a stronger relationship between the manufacturers of chemicals and those who use them. Besides, they appear able to deliver benefits throughout the supply chain as well as wider benefits for society. [27, p. 3]

Chemical leasing

Chemical leasing (ChL) is a preventive and service-oriented business model that shifts away from high sales volumes of chemicals towards an integrated approach and extended producer responsibility throughout the entire life cycle of a chemical. Compared to conventional approaches, the concept of chemical leasing is much more service-oriented. In this business model, the customer pays for the benefits obtained from the chemical, not for the substance itself. Consequently, the economic success of the supplier is not linked to product turnover anymore. The chemical consumption becomes a cost rather than a revenue factor for the chemicals supplier. Companies will try to optimize the use of chemicals and improve the conditions for recycling in order to reduce the amount consumed, which, in turn, reduces the environmental pollution.

Without the ChL model, the appropriate (safe) use and disposal of chemicals would be the responsibility of the user of the chemicals. In the ChL business model, however, this “classical” role allocation is shifted towards the producer and provider of chemicals and the function performed by these chemicals, respectively. The responsibility of the producer and service provider is extended and may include the management of the entire life cycle.

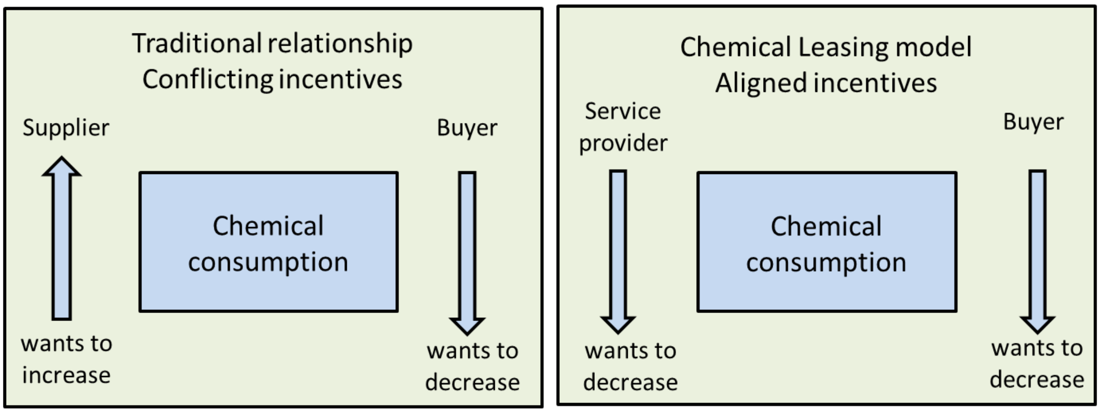


Figure 4-1: Traditional approach vs. chemical leasing model [based on 27, p. 9]

In Europe, the REACH regulation[1] has given a new legislative frame to the production, marketing and usage of chemicals. For certain hazardous chemicals (for example trichloroethylene), it requires authorization processes as a precondition of continued use. In this context, chemical leasing will play an increasingly important role in authorization processes because the business model requires the manufacturers to extend their responsibility and commitment to the safe and optimized use of chemicals. It is expected that in the near future certain chemicals requiring authorization will only be sold under a chemical leasing business model.

The following figure shows how technology and process improvements resulting from intensified collaboration can significantly reduce the consumption of chemicals [29]:

---

[1] More information about REACH: http://ec.europa.eu/enterprise/sectors/chemicals/reach/index_en.htm

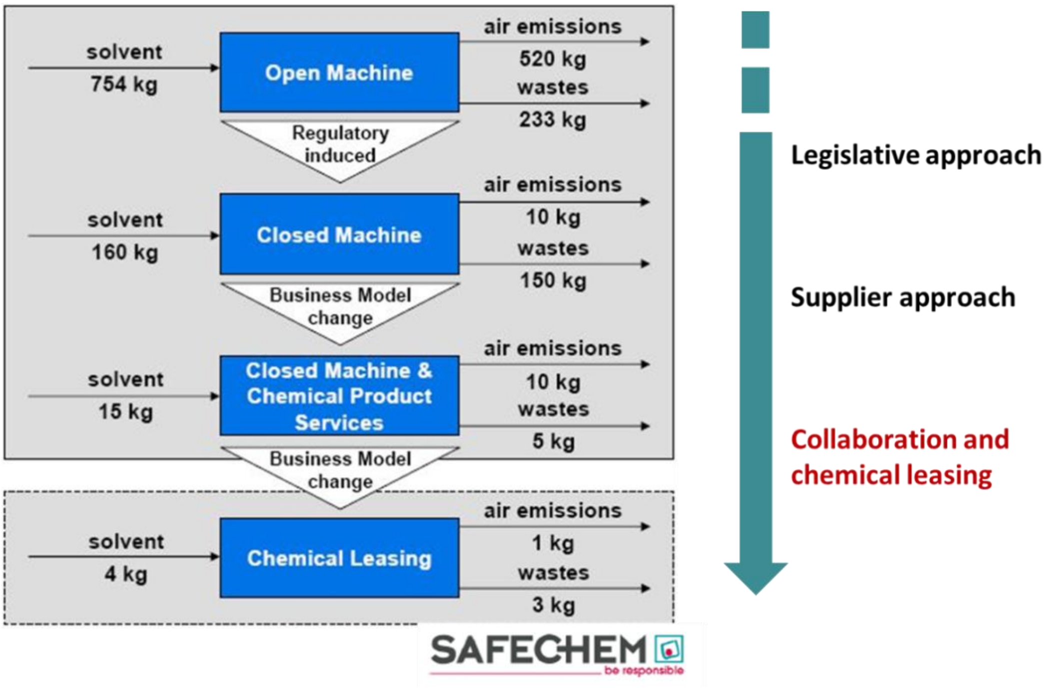


Figure 4-2: Example of consumption and emission reduction by technology and process improvements resulting from intensified collaboration [73 and SAFECHEM Europe GmbH]

The application of ChL models achieves economic advantages for all partners involved, provides specific solutions for efficient chemicals management and ways to reduce negative impacts on the environment. Since chemical products provide a broad variety of services such as “cleaning”, “coating”, “colouring” and “greasing”, the ChL model is applicable in a multitude of industry sectors [30].

Chemical Management Services (CMS)

Chemical Management Services (CMS) is a business model in which a customer purchases chemical services rather than just chemicals. These services can encompass all aspects of the chemical management lifecycle including procurement, delivery/distribution, inventory, use (including chemical substitute research), collection, monitoring/reporting, training, treatment, disposal, information technology and even process efficiency improvements. Each of these services poses its own costs and risks. Under CMS, the service provider is compensated based on the quality and quantity of services provided that reduce lifecycle costs, risks and environmental impacts of a chemical substance, and not on the volume of chemicals sold. Therefore, the service provider has the same objective as the customer: to reduce chemical use and costs. Both partners achieve bottom-line benefits through reduced chemical use, cost and waste. This model is now widely used in the automotive, aerospace and microelectronics sectors, where environmental benefits observed include reduced chemical use, reduced emissions and reduced waste generation, as well as substantial cost savings. A total average cost reduction of 30 per cent has been achieved in the first 5 years [27]. This model differs from ChL in that the unit of payment in ChL is the service provided by the chemical, which will always result in its efficient use, while in CMS the unit of payment is the whole service of chemicals management. This approach depends on the good management of the chemicals by the service supplier.

Closed-loop models

These models take a life cycle approach to materials used in goods and services and furthermore strive to keep materials within the economic system rather than letting them become waste. In the closed loop system, there is effectively no such thing as waste. The application of this approach starts by focusing on what is being delivered to the customer and how it can be achieved more efficiently.

More and more sectors and major businesses are moving towards closed-loop approaches in order to internalize major risks, protect against resource supply disruption, reduce environmental impacts and develop a better value proposition for customers. The benefits of this model are therefore broad and not only environmental in character.

For chemistry-using industries, this approach means not only taking responsibility for minimizing the impacts of the substances produced and sold from raw material sourcing right through to the end of product life, but also taking back the product at the end of its life and restoring it to a condition where it can be reused.

The approach ranges from extending the lifespan of a product (repair and remanufacture) to providing a service based on the effect a substance delivers rather than the substance itself. The latter is typically achieved by full recycling of the material with ownership retained by the provider.

Experience has shown that closed loop models work very well business-to-business but can be harder to implement along complicated supply chains or in business-to-consumer industries [28].

Feedstock foundation

This model focuses on petrochemicals, and typically consists of three to five business units. Feedstock foundation companies produce the essential building blocks for downstream players in the chemical industry and end markets, and concentrate on adding value to feedstock primarily through "smart" locations (advantaged feedstock, growth markets), large-scale facilities and leading process technology [30, p. 4]. Thus, this innovative business model is suitable for limited, large-scale businesses.

Chemicals platform

Chemicals platform companies typically consist of five to ten business units that span the entire chemical value chain. The platform of this model is a sort of "portfolio management company" that concentrates on the businesses, capabilities, markets and products loosely targeted at some of today's mega trends such as health, energy, transportation, housing and construction. These companies consist of a portfolio of business units operating more or less independently according to the companies' governance structure and actively managed for growth and synergy [30, p. 4].

Market maker

Market makers typically consist of one to three business units. This model focuses not on chemical end markets, but rather on selected end markets such as life science, agrochemicals, paints and coatings, and related technologies. Market makers focus on driving innovation based on the understanding of product performance and act on pervasive end-market trends, not simply customer input. These players make a significant investment in brand and distribution. They tend to have high growth with products that represent a limited share of customer cost and value chain [30, p. 4].

4.1.3 Additional sources of information

Websites

Chemical leasing website: a one-stop site to learn everything about this business model and to find helpful guidelines and recommendations for its implementation:
http://www.chemicalleasing.org/index.htm

Material on chemical leasing provided by **UNIDO**: http://www.unido.org/chemical-leasing.html

Chemical Strategies Partnership (CSP) website (USA): provides information on CMS and guidelines for its implementation: http://www.chemicalstrategies.org/implement_manualstools.php

Documents

DEFRA, UK: "A guide to chemical services" (2013); provides an easily accessible introduction to the chemical services model.

EU – DG Environment: "Promoting Innovative Business Models with Environmental Benefits" (2008); describes a selection of innovative business models that are economically profitable and also have positive environmental effects.

4.2 Prevention of major accidents

This chapter provides an overview of the state of the art in the prevention of major accidents, relevant for small and medium enterprises.

4.2.1 Importance of preventing major accidents

The advantages of reducing the likelihood and consequences of major accidents – including better protection of human health, the environment and economic resources – are well known [32, p. 6-7]. An example of legislative measures supporting the prevention of major accidents is the Seveso Directive which obliges Member States of the European Union to ensure that operators have a policy in place to safeguard against major accidents [31].

EC Directive 96/82/EC (Seveso II[2]) definitions [31, article 3]:

Major accident: a major emission, fire or explosion, leading to serious danger to human health and/or the environment, immediate or delayed, inside or outside an establishment, involving one or more dangerous substances

Hazard: an intrinsic property of a dangerous substance, with a potential for harm

Dangerous substances: named substances or substances with certain generic hazardous properties, for example flammability

Community

Major accidents can cause death and serious injury to workers and the local population as well as significant long-term health effects. They can harm livestock, crops and water supplies, and cause considerable environmental damage. They may also result in major economic losses for the enterprise involved and the entire community.

Health and environment

Major accidents can have devastating impacts on human health and the environment. For instance, they can cause direct, immediate harm to workers and other persons in the vicinity who are exposed to the harmful chemicals or who are injured by an explosion or fire. Acute exposure to dangerous substances can also cause long-term health effects including chronic diseases and cancer. Additionally, people may suffer harm indirectly through their diet as a result of ingesting contaminated drinking water, agricultural products, fish, livestock and other food items spoiled by polluted air, surface water and soil.

The release of dangerous substances into the air, water and soil can have serious environmental impacts, killing animals and vegetation, poisoning water supplies used for drinking, fishing and irrigation, and rendering soil unfit for agriculture.

---

[2] The Seveso Directive (currently the Seveso II Directive) will be replaced by the Seveso III Directive on 1 June 2015.

Economic impact

In addition to the potential impact on human health, accidents can cause significant economic harm, both to the enterprise as well as to the community. The costs associated with response, clean-up and recovery, including health services provided such as medical treatment, can be quite significant.

It is obvious that the enterprise where the accident occurred may suffer significant economic losses (from, for instance, property damage, loss of jobs, having to stop operations for an extended period or even bankruptcy). What is less evident are the costs incurred by other industries in the vicinity of the accident. For example, an accident may pollute local water bodies increasing the costs of water used for drinking and agriculture, and causing significant damage to the fishing industry. In addition, suppliers and customers of the enterprise will be impacted.

4.2.2 Main cause of major accidents

The potential for major accidents has become more significant with the increasing production, storage and use of dangerous substances. Inadequate management is often recognized as the main cause of major accidents, specifically:

- Inadequate design;
- Inadequate maintenance and operation procedures;
- Inadequate assessment of the existing hazards and the associated risks in the facility;
- Inadequate staffing or training.

A detailed analysis of an accident will normally reveal three cause levels: basic, indirect and direct (Figure 4-3).

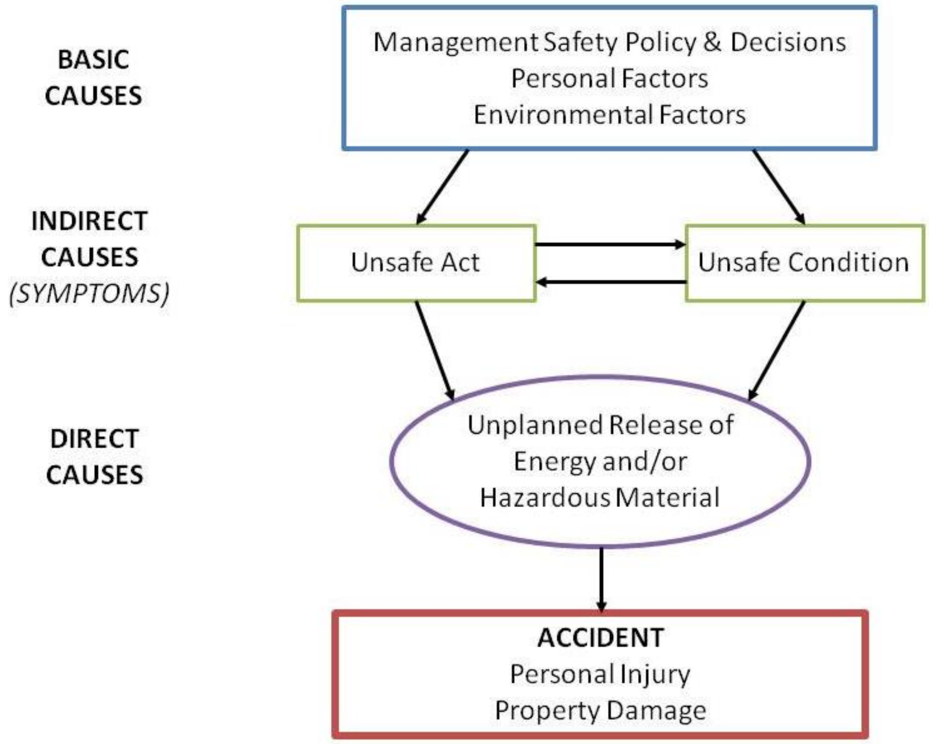


Figure 4-3: The three cause levels of an accident [based on 35, p. 350]

4.2.3 Motivation of SMEs and prevention of major accidents

Measures to prevent major accidents could lead to improved efficiency and lower production costs, as well as to improvements in the general health, safety and environmental performance of enterprises. Safe operations also protect the good will and reputation of industry, and foster improved relationships with members of the local communities.

At the local level, creating an effective major accident prevention plan might result in significant political implications. This could provide a platform for improving communication and trust between local leaders, the public and other stakeholders. Furthermore, communities typically blame local leaders for accidents if there has not been adequate warning or appropriate response.

4.2.4 Prevention of major accidents

Facilities that handle chemicals are actively engaged in dealing with risks to ensure the safety of their workers and their community. Most of their efforts focus on ensuring that the facility is designed and operated safely on a daily basis, using well-designed equipment, preventive maintenance, up-to-date operating procedures and well-trained staff [35, p. 343].

It is recognized that the safe functioning of an enterprise depends on its overall management. Within this overall management system, the safe operation of an enterprise requires the implementation of a system of structures, responsibilities and procedures with the appropriate resources and technological solutions available [32, p. 6-7].

Each enterprise should establish and implement a major accident prevention policy, which provides a basis for major accident prevention in order to minimize the likelihood of an accident and to protect human health, the environment and property. The elements of the safety management system (SMS) should be appropriate to the nature and extent of risks posed by hazardous installations and take the available resources into account [32, p. 92-95].

A safety management system should address[3] the organizational structure, practices, procedures and resources for implementing the major accident prevention policy and should include at a minimum the following items:

- Organizational structure (including roles, responsibilities, training, education, qualifications and inter-relationship of individuals involved in work affecting safety)
- Identification and evaluation of hazards (developing and implementing formal procedures to systematically identify and evaluate hazards – including their likelihood and severity – arising from normal and abnormal operations, and including the hazards arising from handling, production, transportation, storage or disposal of dangerous substances)
- Facilities and operational control (addressing design and construction as well as the procedures for safe operation, including maintenance of plants, processes, equipment and temporary stops)
- Management of change (planning and controlling changes in various areas such as organization, personnel, plant, processes including prestart-up reviews, maintenance and decommissioning, materials, equipment, procedures, software, design and external circumstances that might affect safety)
- Planning for emergencies (related to developing, adopting, implementing, reviewing, testing and, if appropriate, revising and updating emergency plans)

---

[3] Based on the OECD Guiding Principles for Chemical Accident Prevention, Preparedness and Response (second edition, 2003).

- Monitoring performance (concerning the ongoing assessment of compliance with the safety policy and safety management system, and mechanisms for taking corrective action in the event of non-compliance)
- Audits and reviews (addressing the periodic, systematic assessment of the major accident prevention policy as well as effectiveness and suitability of the SMS)

Guidance for SMEs on specific safety management system elements

Small and medium enterprises (SMEs) are a very important part of the global economy, since they are the source of most growth in employment. They are flexible, adaptable and quick to respond to changes in the marketplace and new opportunities.

But if SMEs are to grow and become sustainable, enterprises must learn to consolidate and improve practices, to become more productive, to manage and mitigate risks more effectively and to understand their value chain and business environment more fully. This is why codes, standards, guidelines and frameworks that bring the experience of major companies to small companies in a useable way are so valuable.

UNEP's Responsible Production (RP) Framework for Chemical Hazard Management provides guidelines for small and medium enterprises. It provides a systematic, continuous improvement approach to chemical safety along the value chain. Moreover, the approach provides technical materials and tools to help SMEs understand hazards, control chemical exposure, reduce the risk of accidents and engage stakeholders [33].

The "Guidelines on a Major Accident Prevention Policy and Safety Management System" published in cooperation with the Major Accidents Hazards Bureau of the European Union provide very good advice on safety management systems. The publication provides guidance and descriptions on what is required by the Seveso II Directive [31].

Guidance on safety management systems

Development of a major accident prevention policy

The development of a major accident prevention document/policy is recommended as best practice. This document is intended to give an overview of how the company ensures a high level of protection for humans and the environment. Furthermore, it should clearly indicate the arrangements, structures and management systems required for each of the seven areas described in more detail further below [34, p. 2].

The safety management strategy defines how safety and health are organized, measured and monitored. The development of a safety policy and safety plan is a key point to ensure that the strategies and procedures are implemented at all levels. All seven elements have to be incorporated into the system, including monitoring, audit and review processes which are essential components of the system [36, p. 5].

Organization and personnel

The safety management system should reflect the top-down commitment and the safety culture of the company's organization, translated into the necessary resources and direct responsibilities of personnel involved in the management of major accidents at all levels in the organization. Furthermore, it is helpful to identify the skills and abilities needed by such personnel, and ensure their provision [33, p. 2].

The responsible production (RP) approach provides a systematic method of mapping key aspects (inputs, outputs, modes of production, stakeholders) related to reducing the risk of accidents. It often involves a quick on-site assessment of the company and consultation with management in order to gain a better understanding of the company's needs, priorities and potential areas for improvement.

Hazard identification and evaluation

Hazard identification and risk assessment are two major elements of the risk management process. They are necessary to be able to make decisions relating to risk, for example in terms of risk avoidance, reduction or transfer, or acceptance of the residual risk.

When undertaking a risk assessment, it is important to carefully consider the various possible approaches and methods available, and choose an approach/method that is appropriate for the particular circumstances, since all approaches/methods have their own strengths and weaknesses and none is perfect.

The methodology used for these processes is known as risk analysis or risk assessment. The spectrum of specific methods is broad and covers various degrees of depth and complexity in the analysis as well as various systems of investigation. Risk assessment methods include hazard mapping, checklists, hazard and operability study (HAZOP), "What if" analysis and risk matrix[4].

Techniques that are recommended for the analysis of major hazards include the "Dow Fire and Explosion Index" [37] and the "TNO Purple Book" (guidelines for quantitative risk assessment) [38]. The Responsible Production Toolkit (UNEP) provides tools which can help SMEs undertake hazard identification and risk assessment including prioritization of the identified risks.

Operational control

The company should prepare, update and keep readily available the information on process hazards, design and operational limits and controls resulting from the hazard identification and risk evaluation procedures. Based on these, documented procedures should be prepared and implemented to ensure the safe design and operation of plants, processes, equipment and storage facilities [33, p. 5].

Straightforward guidelines on how to prepare a company's process flow diagram can be found in the Responsible Production Toolkit. An objective is to clearly map the process flow in order to understand what the activities are and who is involved in them. This will help getting a better understanding of where chemicals are used and located. Process flow means both the sequence of activities that are undertaken in the company and the external activities that the company can influence within its business, ranging from the products and services the company procures to the products and services the company provides [33, p. 14].

Management of change (MOC)

According to the International Social Security Association (ISSA), management of change (MOC) is defined as "a systematic process to ensure the transition from an initially safe state to a new – again safe – state, along a safe path. The new state may be permanent or temporary." In 2007, the ISSA published a practical guidance document on maintenance and changes in plants with high safety requirements [39]. This document is a valuable source for helping companies institute MOC.

Maintenance and changes are part of normal plant operation in the chemical industry, yet serious accidents often occur due to changes in processes. Changes frequently leading to unsafe conditions if not properly analyzed include the change of [39]:

- Construction materials
- Process parameters
- Inerting procedures
- Equipment parameters

---

[4] An overview of the listed methods can be found in UNEP's Flexible Framework for Addressing Chemical Accident Prevention and Preparedness, SG-2 Guidance on Risk Assessment (p. 122-125).

Such changes can be temporary or permanent, small or large. Nevertheless, any changes or modifications that result in deviations from the safety protocols (or safety management plan) are subject to a hazard analysis and risk assessment procedure. This is fundamental to all MOC activities.

According to the ISSA, typical items on a plant change form include:

- Administration (sequential number, date, plant, piping and instrumentation diagram)
- Description of the change (What will be changed? Why? What are the objectives?)
- Additional information (deadlines, cost)
- Schedule including the sequence of work (planning, preparation, main work, auxiliary work, termination) designed so that the work flow clearly appears from the entries
- Document update (P&I sheets, permits, explosion protection documents, safety checks and hazard analyses)
- Checks before start-up (process control system (PCS), pipes, pressure vessels, unloading points and filling stations)
- Approvals (with signature and date)

Further practical information relating to planning changes and accounting for safety in the various phases of changes (i.e. preliminary planning, basic design, detailed design, construction, commissioning and production) are found in the ISSA publication.

The following table provides an overview of MOC requirements according to the US Environmental Protection Agency (US EPA) and can be a useful guideline for implementing a company's MOC policy.

Table 4-1: Management of change requirements, Chapter 7.8 (2004) of the EPA General Risk Management Program Guidance [based on 40]

MOC procedures must address:	**Employees affected by the change must:**	**Update process safety information if:**	**Update operating procedure if:**
Technical basis for the change Impact on safety and health Modifications to operating procedures Necessary time period for the change Authorization requirements for the proposed change	Be informed of the change before start-up Trained in the change before start-up	A change covered by MOC procedures results in a change in any process safety information	A change covered by MOC procedures results in a change in any operating procedure

Emergency planning

The safety management system should include the procedures necessary to ensure that an adequate emergency plan is developed, adopted, implemented, reviewed, tested, and, where necessary, revised and updated. The company should develop and maintain procedures to identify foreseeable emergencies arising from its activities, identified through hazard and risk assessment, and to record this analysis and keep it up-to-date. Plans to respond to such potential emergencies should be prepared, and arrangements for testing and review on a regular basis should be included within the SMS. The procedures should also cover the necessary arrangements for communicating the plans to all those likely to be affected by an emergency [34, p. 6].

Proper assessments can only be made by undertaking a detailed safety and risk assessment audit of the operations, worker practices, company policies and the workplace environment [35, p. 418]. Section 3 of the Responsible Production Toolkit gives recommendations on how to respond to the hazards and risks identified through reviewing the company's processes and activities. Furthermore, it provides guidelines on how to develop an appropriate response to chemical hazard issues and the associated impacts and how to communicate them to the concerned community. There are also a number of international publications that provide guidance on emergency planning related to major accidents, some of them being listed in the following paragraph.

4.2.5 Additional sources of information

Websites

Health and Safety Executive (**HSE**), UK website: provides a wealth of information and advice on work-related health and safety and the prevention of accidents: http://www.hse.gov.uk/

UNEP Safer Production website: provides a list of additional resources related to safer production: http://www.unep.org/resourceefficiency/Business/CleanerSaferProduction/SaferProduction/AdditionalResources/tabid/101149/Default.aspx

Documents

European Commission, Major Accidents Hazards Bureau (**MAHB**): "Guidelines on a Major Accident Prevention Policy and Safety Management System"

OECD: "Guiding Principles for Chemical Accident Prevention, Preparedness and Response" (second edition, 2003)

GTZ: **"**Chemical Management Guide for Small and Medium-Sized Enterprises" (2007).

UNEP: "Responsible Production Booklet; A Framework for Chemical Hazard Management for Small and Medium-Sized Enterprises" (2009).

European Process Safety Centre (**EPSC**): "HAZOP: Guide to Best Practice" (second edition, 2008)

4.3 Safe handling of chemicals

This section provides a brief overview of:

- Hazards associated with the use and handling of chemicals
- Hazard communication in the form of labels and SDSs
- Performing a basic risk analysis
- Developing workplace operating instructions based on SDSs
- Preventive measures including:
    - Hierarchy: elimination, substitution, control: TOP hierarchy
    - COSHH Essentials Toolkit or ILO Toolkit (focus on essentials)

Chemicals are used in virtually all work activities, thus presenting certain chemical risks in a large number of workplaces all over the world. Many thousands of chemicals are used in substantial quantities, and many new chemicals are also introduced on the market every year. Hence, there is an urgent need to establish a systematic approach to safety in the use of chemicals at work.

An effective control of chemical risks at the workplace requires an efficient flow of information on potential hazards and the safety precautions to be taken from the manufacturers or importers of chemicals to the users. Employers should follow up on this information and ensure on a day-to-day basis that the necessary measures are taken to protect workers, and consequently the public and the environment.

Chemicals can be corrosive, reactive, flammable, explosive, oxidizing and inert, and contribute to serious health effects such as burns, rashes, kidney damage, lung damage, heart conditions, cancer, damage of the central nervous system, etc.

Routes of occupational exposure include:

- Inhalation: Nearly all materials that are airborne can be inhaled. This is the most common route. Gases and vapours can pass into the blood whereas solid particles are inhaled into the lungs.
- Dermal absorption: Skin contact with a substance can result in a possible reaction and many solids, liquids, vapours and gases can be absorbed through the skin.
- Ingestion/swallowing: Workers do not deliberately swallow materials they handle, however, the failure to wash hands, or eating in the presence of chemicals can lead to ingestion.
- Injection: Though uncommon, accidents occurring during the handling of sharp objects can result in the injection of a chemical into the bloodstream.
- Ocular: Chemicals are absorbed through the eyes or cause physical damage.

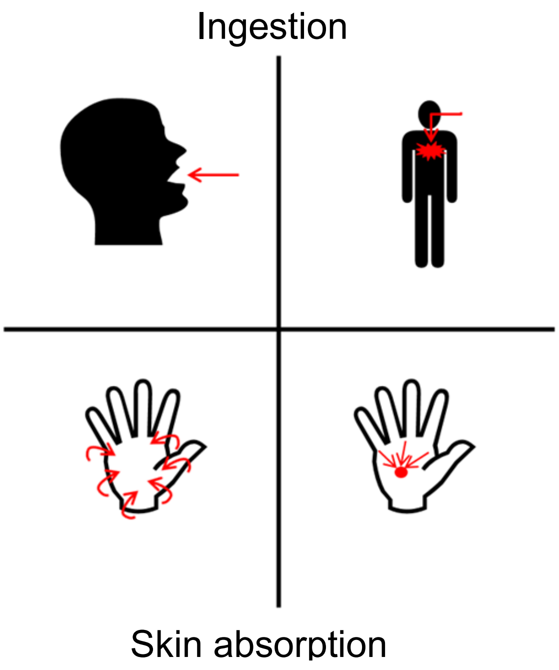


Figure 4-4: Routes of occupational exposure [1]

The safe use of chemicals involves several building blocks in which the GHS is a key element (see the following sub-chapter).

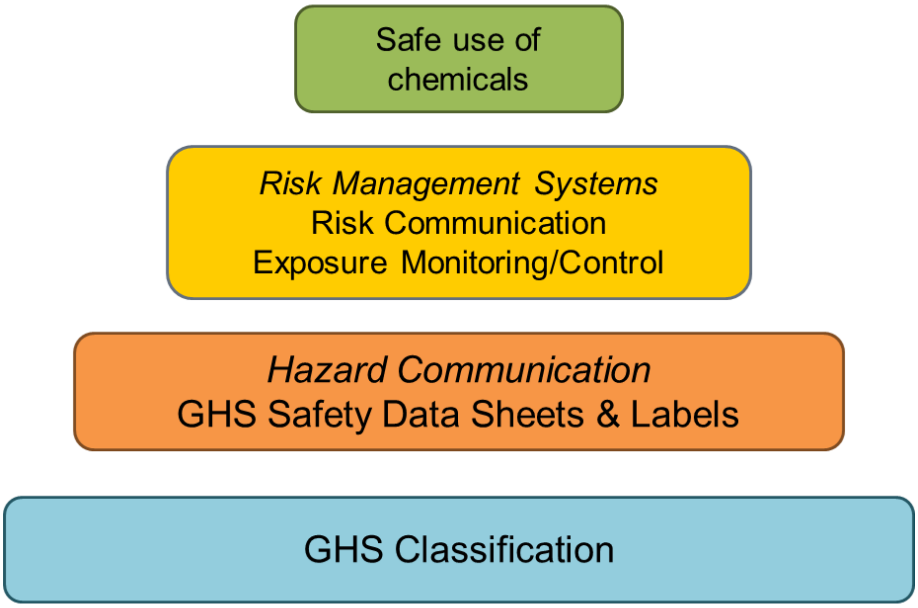


Figure 4-5: Building blocks for the safe use of chemicals

4.3.1 Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is an internationally agreed-upon system, created by the United Nations. The GHS is a worldwide initiative to promote standard criteria for classifying chemicals according to their health, physical and environmental hazards. It is an international approach to hazard communication, providing agreed criteria for the classification of chemical hazards, and a standardized approach to label elements and safety data sheets (SDSs). The primary goal of the GHS is better protection of human health and the environment by providing chemical users and handlers with enhanced and consistent information on chemical hazards [41, p. 63].

It is important to note that the GHS is currently being implemented in many countries, which means that users of chemicals will still encounter systems currently used in many major chemical producing countries.

The key elements of GHS include:

- Harmonized classification criteria
- Harmonized labelling elements
- Harmonized safety data sheet elements

The GHS uses the **signal words** “Danger” and “Warning”, **pictograms**[5]**, hazard statements**, and **precautionary statements** to communicate hazard information on product labels and safety data sheets.

---

[5] Note: Not all categories have a symbol associated with them

Hazard classification

The GHS distinguishes three major hazard groups:

- Physical hazards
- Health hazards
- Environmental hazards

Each hazard group consists of classes and categories (sub-sections of classes). For example, the hazard class "self-reactive substances and mixtures" has seven hazard categories (A-G). In general, the hazard categories are either in numerical or alphabetical order with "1" or "A" representing the most hazardous category.

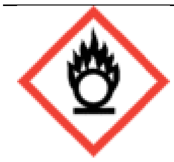
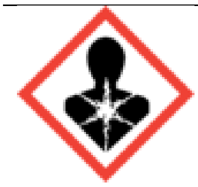
Table 4-2: Hazard classification [based on 49]

Classes in the group "Physical Hazards"	
• Explosives • Flammable gases • Aerosols • Oxidizing gases • Gases under pressure • Flammable liquids • Flammable solids	• Self-reactive substances and mixtures • Pyrophoric liquids • Pyrophoric solids • Self-heating substances and mixtures • Substances and mixtures which, in contact with water, emit flammable gases • Oxidizing liquids
Classes in the group "Health Hazards"	
• Acute toxicity • Skin corrosion/irritation • Serious eye damage/eye irritation • Respiratory or skin sensitization • Germ cell mutagenicity • Carcinogenicity	• Reproductive toxicity • Specific target organ toxicity – single exposure • Specific target organ toxicity – repeated exposure • Aspiration hazard
Classes in the group "Environmental Hazards"	
• Hazardous to the aquatic environment (acute and chronic)	• Hazardous to the ozone layer

The following figure presents an overview of the pictograms used in the GHS and the UN Model Regulations on the Transport of Dangerous Goods (UNTDG) and their meanings.

Table 4-3: Pictograms used in the GHS and the UN Model Regulations on the Transport of Dangerous Goods (UNTDG) [based on 50]

Hazard pictogram	GHS hazard	Dangerous class labels (pictograms)	Dangerous good classes
	Explosive Self-reactive Organic peroxides		Explosive

Hazard pictogram	GHS hazard	Dangerous class labels (pictograms)	Dangerous good classes
	Flammable Self-reactive Pyrophoric Self-heating Emits flammable gas in contact with water Organic peroxides		• Flammability (liquid, solid or gas) • Pyrophoric • Emits flammable gas • Organic peroxide
	Oxidizers		• Oxidizer • Oxidizing gas
	Gases under pressure		• Non-toxic non-flammable gas • Flammable gas • Oxidizing gas • Toxic gas
	Acute toxicity		• Acute toxicity • Acute toxic gas
	Acute toxicity Skin irritant Eye irritant Skin sensitizer	No equivalent	
	Carcinogen Respiratory sensitizer Reproductive toxicant Germ cell mutagen	No equivalent	

Hazard pictogram	GHS hazard	Dangerous class labels (pictograms)	Dangerous good classes
	Eye corrosion Skin corrosion Corrosive to metal		Corrosive to metals
	Aquatic toxicity Not covered within the scope of workplace hazardous chemical requirements		Environmental hazard

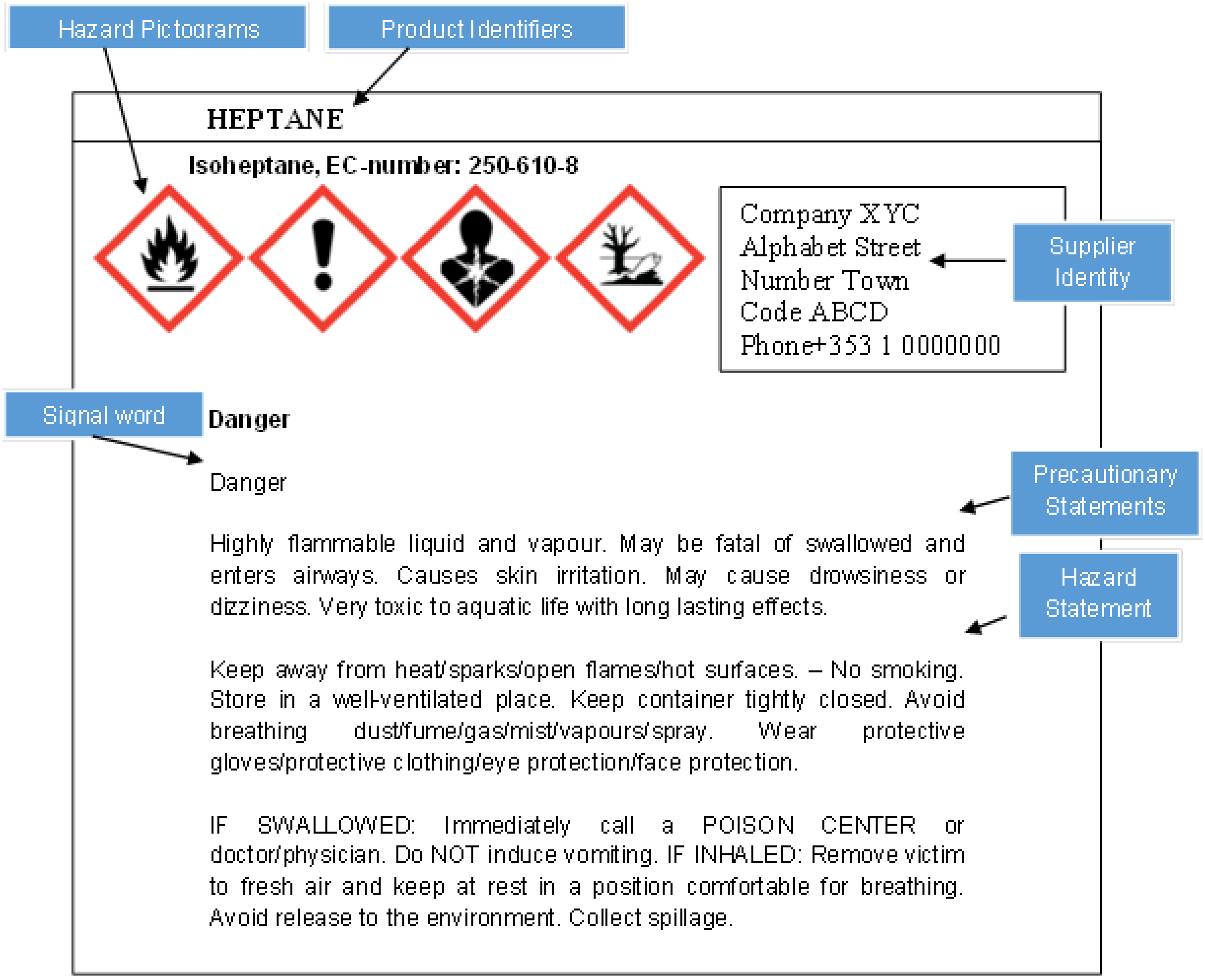
Labelling

A label is the key to organizing chemical products for storage. Tanks, containers and bulk stores should be identified and marked with signs indicating the name/identity of the chemical product. The labels must be comprehensive and easily understandable to provide full information about each class and category of hazards according to the GHS.

Containers (including cylinders of compressed gases) must not be accepted without the following identifying labels:

- Identification of contents (for example chemical name)
- Description of principal hazards (for example flammable liquid)
- Precautions to minimize hazards and prevent accidents
- Appropriate first aid procedures
- Appropriate procedures for cleaning up spills
- Special instructions to medical personnel in case of an accident

Below, a model label is shown as adopted by the EU Classification, Labelling and Packaging Regulation (CLP Regulation), which aligns EU legislation to the GHS.



HEPTANE

Isoheptane, EC-number: 250-610-8

Company XYC
Alphabet Street
Number Town
Code ABCD
Phone+353 1 0000000

Danger

Danger

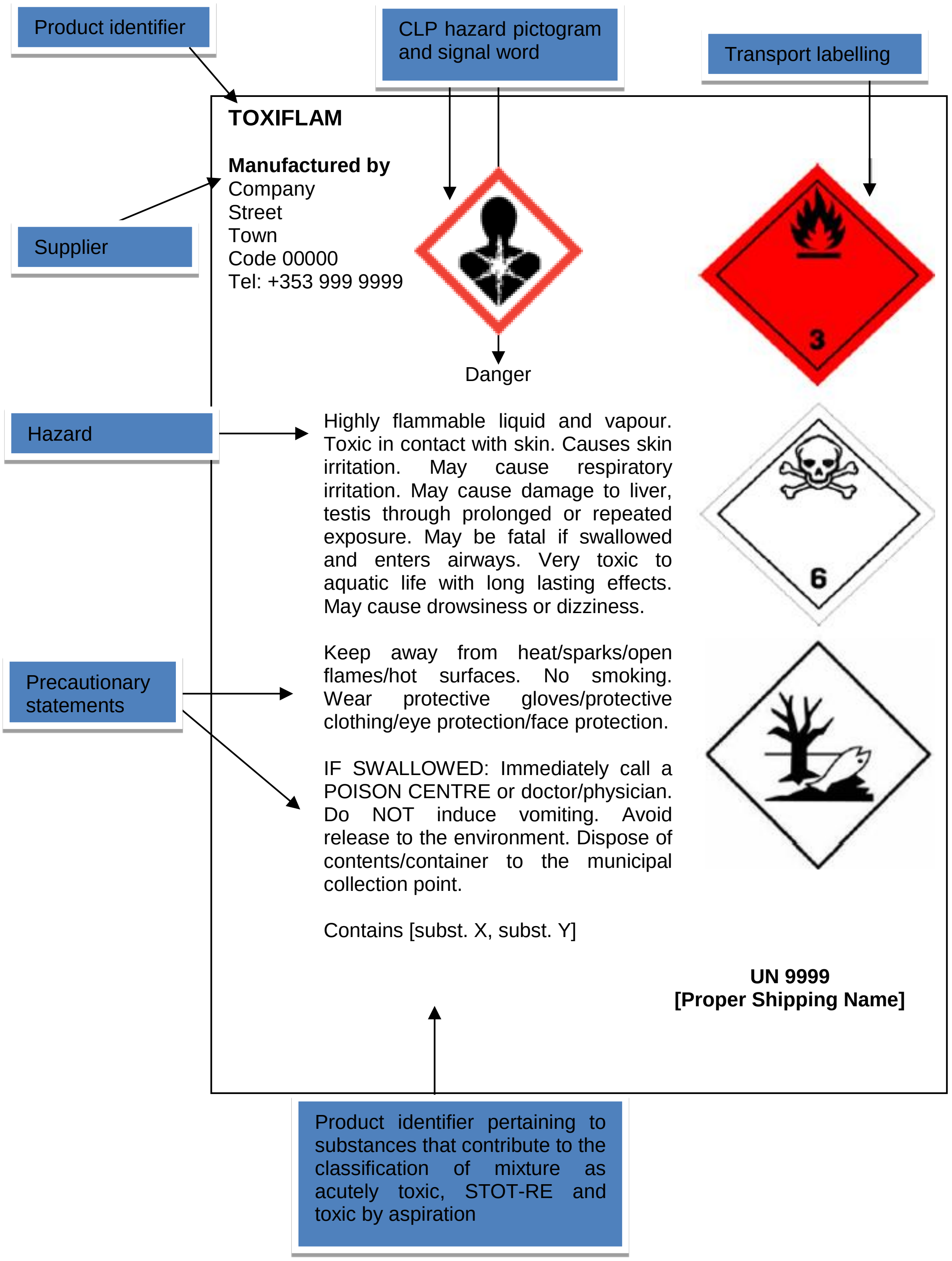
Highly flammable liquid and vapour. May be fatal of swallowed and enters airways. Causes skin irritation. May cause drowsiness or dizziness. Very toxic to aquatic life with long lasting effects.

Keep away from heat/sparks/open flames/hot surfaces. – No smoking. Store in a well-ventilated place. Keep container tightly closed. Avoid breathing dust/fume/gas/mist/vapours/spray. Wear protective gloves/protective clothing/eye protection/face protection.

IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician. Do NOT induce vomiting. IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing. Avoid release to the environment. Collect spillage.

Figure 4-6: Model label according to the EU CLP (harmonized with GHS) [based on 49]

Additionally, a label for combining transport pictograms and GHS requirements is shown.



TOXIFLAM

Manufactured by
Company
Street
Town
Code 00000
Tel: +353 999 9999

Highly flammable liquid and vapour. Toxic in contact with skin. Causes skin irritation. May cause respiratory irritation. May cause damage to liver, testis through prolonged or repeated exposure. May be fatal if swallowed and enters airways. Very toxic to aquatic life with long lasting effects. May cause drowsiness or dizziness.

Keep away from heat/sparks/open flames/hot surfaces. No smoking. Wear protective gloves/protective clothing/eye protection/face protection.

IF SWALLOWED: Immediately call a POISON CENTRE or doctor/physician. Do NOT induce vomiting. Avoid release to the environment. Dispose of contents/container to the municipal collection point.

Contains [subst. X, subst. Y]

UN 9999
[Proper Shipping Name]

Figure 4-7: Label for combining transport pictograms and GHS requirements [based on 49 and 50]

GHS safety data sheets

The GHS safety data sheets are key documents in the safe supply, handling and use of chemicals. They should provide comprehensive information about a chemical product that allows employers and workers to obtain concise, relevant and accurate information on the hazards, uses and risk management associated with the substance in the workplace.

An SDS provides the following information:

- Substance properties
- Health, environmental and physical-chemical hazards
- Storage, handling, transportation and final disposal
- Safety instructions for workers and measures to be taken in the event of a fire or accidental release as well as first aid procedures.

Based on this information, a hazard analysis is drawn up and workplace operating instructions are provided.

The SDS should contain 16 sections: [42, p. 5-9, p. 39]

- Identification
- Hazard(s) identification
- Composition/information on ingredients
- First-aid measures
- Fire-fighting measures
- Accidental release measures
- Handling and storage
- Exposure control/personal protection
- Physical and chemical properties
- Stability and reactivity
- Toxicological information
- Ecological information
- Disposal considerations
- Transport information
- Regulatory information
- Other information

In many countries, the chemical producer is under legal obligation to provide an SDS. If the SDS is not delivered together with the chemical or provided electronically, the downstream user should request the SDS from the supplier (always the latest version).

Further information on the preparation of SDSs in compliance with the GHS was developed by the European Chemicals Agency (ECHA) and can be found in the section “Additional sources of information” further below. An example of an SDS complying with the EU CLP legislation is provided on the website indicated below[6].

4.3.2 Hazard identification and risk analysis

The following section is based on UNEP’s Responsible Production Approach [43].

Understanding your operational processes

“Hot spots” are defined as:

- Places where you can observe inefficient handling or use of chemicals
- Particularly hazardous situations where chemicals are being stored or used and where the potential harm could be reduced or prevented by implementing appropriate control measures

To identify hot spots, you need to look at your operations in a different way. Rather than focusing on the end product, you need to look in a detailed way at the storage, handling and use of chemicals in the production process. Look specifically at how chemicals are being treated in steps involving their purchase, storage, handling and processing with the aim of spotting inefficiencies, waste, losses and risks. [44, p. 20]

The hazard analysis should not only focus on production but include cleaning operations (cleaning of reactors and equipment), maintenance activities (preventive and corrective) and start-up/shut-down procedures.

---

[6] http://reachteam.eu/english/compliance/SDS/docs/CLP_REACH_Compliant_SDS.html

Drawing up a chemical process flow diagram

The objective is to clearly map the process flow of chemicals in order to understand what the activities are and who is involved in them. This will help you to understand where chemicals are used and located (chemical streams). [43, p. 14-15]

The basic strategy for a block flow diagram preparation is:

1. List all the steps and activities in the process.
2. Arrange the activities in sequence.
3. Discuss the sequence of activities with the relevant people in your company.
4. Review the flowchart with your workers and your business partners.
5. Check to see if they agree that the process has been drawn accurately.

Identification of chemicals, their quantities and the hazards involved in the process

The next step is to identify chemicals, their quantities and the hazards associated with their use at the company. It is important to identify the hazards for all chemicals involved in the process [43, p. 14-15].

The objective is to systematically identify all chemical substances that are stored, handled and used at your business, along with information on their quantities and type of storage, and to classify them according to chemical product information, labels and GHS safety data sheets. Check this against the process flows to make sure you have not missed anything. Establish what information already exists within the company regarding chemicals (for example, purchasing records, stock control cards, inventories, suppliers' product information, GHS SDSs, etc.). List all chemical substances in an *inventory*. Begin with one department or process and proceed on a step-by-step basis until you have a complete inventory for your whole operation [45, p. 16].

Assessing health, environmental and economic risks

Tool 1.3 of the Responsible Production Toolkit provides a methodology to estimate the impact and likelihood of an accident situation. Note that the assignment of both the severity of impact and the likelihood of occurrence are *subjective* decisions, and therefore a multi-disciplinary team should be involved. The rating of the severity of a hazard should be based on the hazard and precautionary statements outlined in the SDS (hazard and precautionary statements are found in section 2 of the GHS SDS template). Further information on physical and chemical properties, stability and reactivity as well as health effects can be found in sections 9 to 11 of the GHS SDS template.

An essential component to assessing chemical risks is the creation of a compatibility matrix of hazardous substances. This tool can assist in determining the chemical reactivity of substances and mixtures (for example, toxic by-products or extreme heat generation). The Chemical Reactivity Worksheet[7] predicts possible hazards resulting from the mixing of hazardous substances (chemicals) as well as data on whether the substance reacts with air, water or other materials. This hazard information can be entered in the risk matrix of the Responsible Production Toolkit.

4.3.3 Preventive and protective measures

Once you know where the chemicals are, what kind of chemicals you are handling and what their hazards are, you can use a hierarchy of controls to choose the best way of handling the chemicals safely as shown in the figure below.

---

[7] The Chemical Reactivity Worksheet can be downloaded at: http://response.restoration.noaa.gov/oil-and-chemical-spills/chemical-spills/response-tools/downloading-chemical-reactivity-worksheet.html

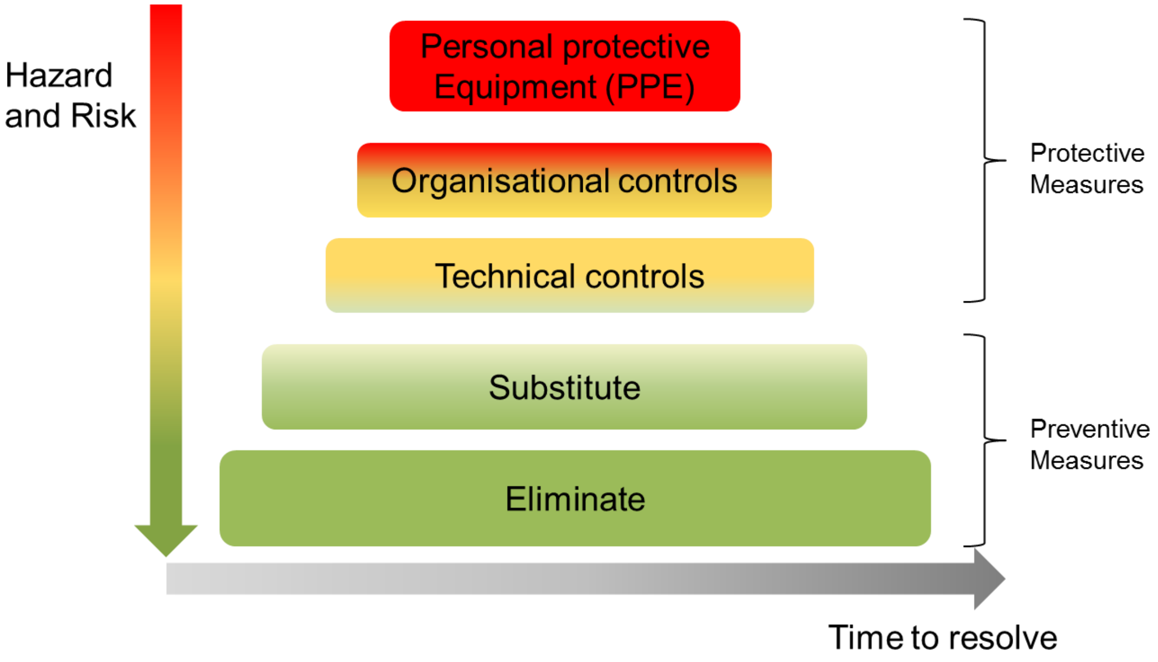


Figure 4-8: Hierarchy of steps according to the control strategy [based on 45, p. 22]

Preventive measures

Before the materials discarded from a process or a part thereof become waste, there are some measures that can be taken in order to prevent this conversion.

Eliminate

If you are not using a hazardous chemical, then there is no risk. Eliminating the hazardous chemical is the best way to control the risk. Consider whether you really need to use a chemical at all. For example, in recent years paint manufacturers have been able to eliminate hazardous solvents such as xylene [46, p. 23]. You could also consider whether it is possible to use a different process which does not require a hazardous chemical.

Substitute

It may be possible to replace your hazardous chemical by a less hazardous one. For example, you could replace isocyanate-based paints by water-based paints. You could also use a less hazardous form of the same chemical, For instance, using the chemical in pellet form rather than the powder could have a significant effect on reducing inhalable dust levels [46, p. 23]. It is important that you consider hazards and potential exposure associated with the replacement chemical to ensure that no new hazard is introduced to the workplace.

The CatSub database (www.catsub.eu) provides a publicly accessible catalogue of more than 300 examples of substitution of hazardous chemicals including case studies that describe successful substitutions with less hazardous chemicals or hazard-free products. Furthermore, the European Agency for Safety and Health at Work provides some factsheets to support in the substitution of hazardous chemicals (Factsheet 34 – Elimination and substitution of dangerous substances[8]).

---

[8] See http://osha.europa.eu/en/publications/factsheets/34

The internet portal SUBSPORT[9] (SUBStitution Support PORTal – Moving Towards Safer Alternatives) combines information from several countries (for example, Denmark, Germany, Spain, Sweden and the USA) regarding tools and case studies for the substitution of hazardous substances in products and processes with less hazardous alternatives. The portal is available in English, French, German and Spanish.

Protective measures

Protective control measures can be subdivided into the following TOP hierarchy:

- Technical control measures
- Organizational control measures
- Personal protective equipment

Technical control measures

Technical control measures are designed to move an air contaminant away from personnel and/or to create a barrier between a hazard and the employee. Some common types of engineering control measures are discussed below [46, p. 2-3].

Chemical fume hoods

Chemical fume hoods are the primary containment devices used to protect personnel and the laboratory environment from hazardous chemicals that may become airborne through volatilization or aerosol formation.

Use a chemical fume hood when working with

- Flammable liquids
- Particularly hazardous substances that are volatile or that are in powder form
- Other volatile compounds
- Chemicals with a strong odour
- Other materials as indicated by the chemical- or lab-specific standard operating procedure

Local exhaust ventilation

Local exhaust ventilation is used with a localized source of chemical vapours that can be captured. Examples include snorkel-type exhaust and downdraft sinks. Local exhaust ventilation should only be installed with the involvement of the facility management for your building.

Isolation devices

These devices physically separate a contaminant-generating process from the work environment. They will often involve a sealed plexiglass box, and may be combined with local exhaust.

Process modification

Process modification involves changing the temperature or pressure at which a process is conducted, or using inert gas, or any other change in the procedure to reduce the likelihood of exposure or incidents.

Organizational control measures

The use of management and administrative procedures aims to reduce or eliminate exposure [41, p. 24].

Look how the work is done and consider how employees are exposed to the chemical. Think about how the job could be done differently to avoid exposure. Where it is not possible to eliminate or

---

[9] http://www.subsport.eu/

isolate the chemical hazard, you should minimize exposure to it. This can be achieved by introducing written procedures in your workplace to:

- Minimize the number of employees who might be involved in a task, for example by introducing job rotation
- Exclude other employees not involved in the task from the area where the chemical is being used
- Provide training to your employees on the hazards and safe use of the chemicals they work with
- Ensure chemicals with hazardous properties are correctly stored
- Ensure emergency procedures are in place in the event of an accident, for example spillage

These procedures should be known by and available for all organizational levels.

Note: The posting of *operational procedures* highlighting the necessary precautions and methods of handling chemicals for certain tasks can help reduce the risk of accidents. The operational procedures (or working instructions) should contain the following sections: identification of the hazardous substances, hazards to human health and the environment, protective measures and rules of conduct, conduct in the event of danger, first aid and proper disposal. An example of how to obtain working instructions out of an SDS can be found in the annex of the document available at the link indicated below[10].

Personal protective equipment (PPE)

The use of personal protective equipment (PPE) should be the last line of defence and not regarded as an alternative to other suitable control measures which are higher up the hierarchy. It should provide adequate protection against the risks arising from the hazardous chemicals to which the wearer is exposed, for the duration of the exposure, taking into account the type of work being carried out. [41, p. 27]

Section 8 of the GHS SDS gives advice on steps needed to reduce exposure, including advice on appropriate PPE. Examples of precautionary pictograms to be included on an operational procedure sign are shown in the figure below:

Figure 4-9: GHS precautionary pictograms [based on 49]

Personal protective equipment can include:

- Eye/face protection (for example safety glasses, goggles, face shields)
- Skin protection (for example chemical-resistant footwear including shoes, boots and rubber boots, and clothing such as aprons or suits)

---

[10] http://www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/TRGS/pdf/TRGS-555.pdf?__blob=publicationFile&v=2

- Hand protection (for example gloves or gauntlets, disposable or otherwise, that are suitable for the task)
- Respiratory protection (for example respirators, masks or hoods that give adequate protection)
- Thermal protection (employees may need to be protected from excess heat or cold with appropriate clothing)

There are several methods for determining the level of protection for PPE in the workplace. The US agency OSHA defines the four levels A, B, C and D, with A signifying the highest level of protection for skin and respiratory safety in the workplace. The method for determining the level of protection and the following table are provided in chapter 5 of the book "Practical Guide to Industrial Safety" [35].

Table 4-4: Level of protection and corresponding required personal protective equipment [based on 35]

Personal protective equipment	Level of protection			
	A	B	C	D
Hard hat	■	■	■	■
Face shield or safety glasses			■	■
Boots	■	■	■	■
Inner gloves	■	■	■	
Outer gloves	■	■	■	
Work coveralls				■
Chemical-resistant coveralls			■	
Chemical-resistant suit		■		
Fully encapsulating suit	■			
Air purifying respirator			■	
SCBA (self-contained breathing apparatus)/airline respirator	■	■		
Two-way radio	■			
Cooling system	■			

OSHA provides online tools to help in the selection of appropriate protective equipment, including eye and face protection[11] and respiratory protection[12]. Furthermore, most suppliers provide the ability to search appropriate PPE according to an identified chemical.

Contractors' and maintenance activities

Two additional sources of accidents that are often neglected are *contractors'* and *maintenance activities* (preventive and corrective). Regular servicing and maintenance work is required due to the high stress placed on equipment in the chemical industry by exposure to very aggressive substances. Three kinds of maintenance work may be identified in the chemical industry: ongoing or daily maintenance work (executed without shutdown of the installation but where the equipment may be isolated), maintenance with a shutdown of the installation, and modification or construction of new units. Subcontractors may be involved in all three kinds of maintenance work. Outsourcing maintenance work is becoming the norm in the chemical industry.

---

[11] https://www.osha.gov/SLTC/etools/eyeandface/index.html

[12] https://www.osha.gov/SLTC/etools/respiratory/index.html

In many countries, the company has legal responsibility for the safety of any personnel working within its installations, including contractors and external workers (revise local regulations carefully). Therefore, any occupational safety and health (OSH) management plan should include contractors and maintenance activities. Several fact sheets are available from the European Agency for Safety and Health at Work (EU-OSHA) to assist companies in integrating maintenance activities and any related (sub)-contracting[13].

4.3.4 Online tools for controlling health risks from chemicals: COSHH Essentials

The COSHH Essentials website[14] provided by the UK Health and Safety Executive is similar to the ILO International Chemical Control Toolkit[15], but it goes a step further and provides direct guidance based on input to an interactive website. After entering data of processes and operations in the online tool[16], users are given advice on a range of tasks involving chemicals, such as mixing or drying.

Details on relevant control measures such as “drum emptying” or “transferring liquid by pump” are available for download and are valuable tools for protecting workers.

4.3.5 Additional sources of information

Websites

UNECE (United Nations Economic Commission for Europe): provides more information about the GHS and the application of the GHS criteria:
http://www.unece.org/trans/danger/publi/ghs/guidance.html

HSE (Health and Safety Executive): UK website providing a wealth of information and advice on work-related health and safety, and guidance on the control of hazardous substances:
http://www.hse.gov.uk/

Documents

UNEP: Responsible Production Handbook. A Framework for Chemical Hazard Management for Small and Medium Sized Enterprises

HAS (Health and Safety Authority), Ireland: Your steps to chemical safety. A guide for small business

GTZ Chemical Management Guide for Small and Medium Sized Enterprises, 2007

4.4 Storage of hazardous chemicals

All substances or mixtures presenting one or several hazards that could have adverse effects on humans’ and animals’ health or life, harm the environment or damage infrastructures are considered as hazardous materials. The presence of these substances in a company requires special rules for handling, processing, disposal and, of course, for storage. The aim of this chapter is to present general

---

[13] https://osha.europa.eu/en/publications/e-facts/e-fact-62-safe-maintenance-working-with-contractors-and-subcontractors/view ; https://osha.europa.eu/en/publications/e-facts/e-fact-66-maintenance-and-hazardous-substances/view ; https://osha.europa.eu/en/publications/e-facts/e-fact-67-maintenance-chemical-industry/view

[14] http://www.hse.gov.uk/coshh/essentials/index.htm

[15] http://www.ilo.org/legacy/english/protection/safework/ctrl_banding/toolkit/icct/

[16] http://www.hse.gov.uk/coshh/essentials/coshh-tool.htm

and specific rules for the storage of hazardous substances in order to prevent fires, explosions, the formation of gases and toxic vapours, the pollution of soils, surfaces and groundwater, etc.

The literature is rich with information, and it is not possible to provide here an exhaustive list of the standards regarding the storage of hazardous substances. The objective of this chapter is to present the most relevant rules, applicable in an industrial context, in order to enable the safety manager (or equivalent) to analyze the storage conditions in the company, identify gaps and define where measures need to be taken to ensure compliance with standard storage policies. However, it is important to keep in mind that national regulations and safety values have to be complied with at any time.

4.4.1 Storage concept

A storage concept includes all the relevant information needed to ensure the safe storage of hazardous materials and compliance with regulations as well as environmental and safety requirements. It gives an overall view of the local situation and available measures. By drawing up a storage concept, the following objectives can be achieved [47]:

- The local conditions and measures are perfectly adapted to the hazards arising from the stored products.
- As a result of the overall consideration, conflicting measures are identified and may be adjusted.
- Legal requirements are met.

To achieve these goals, a storage concept must include the following information:

- A description of the local environment including storage conditions, physical properties of storage rooms and definitions of the stored substances
- The nature and the quantity of the hazardous substances
- Structural, technical and organizational measures

4.4.2 Classifications/categories

Hazards

The hazards associated with chemical substances were presented in the previous chapters of this manual. The various properties need to be described in safety data sheets and other relevant documents, and marked on containers. The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is a standardized system to classify substances and hazards and was covered in Section 4.3.1, where the different hazards and their pictograms were described.

Storage classes (SC)

Based on the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) [51] and the UN Recommendations on the Transport of Dangerous Goods [50], nine material classes (and additional subclasses) were defined, for which specific handling and storage rules were developed. Three of them are not dealt with here as they are too specific (infectious, radioactive and explosive materials). The categories are listed in the following table.

Table 4-5: Storage classes [based on 50 and 51]

Storage class	Substance properties	ADR/UN labelling	GHS labelling
SC 2	Liquefied gases or gases under pressure		
SC 3	Flammable liquids		
SC 4.1	Flammable solids		
SC 4.2	Substances liable to spontaneous combustion (auto-flammable)		
SC 4.3	Substances which, in contact with water, emit flammable gases		
SC 5	Oxidizing substances/organic peroxides		
SC 6.1	Toxic substances		
SC 8	Corrosive or caustic substances		
SC 9	Miscellaneous dangerous substances and articles, including environmentally hazardous substances		

Examples of hazardous substances and their reactions

As a general rule, the storage of chemicals must be organized in different areas, according to the storage classes defined above. Moreover, possible chemical reactions between substances that can be severe and dangerous have to be considered, for instance:

- When acids react with non-precious metals (aluminium, silicon, zinc or iron) or when alkali metals (sodium or potassium) come into contact with water, or just humidity from ambient air, hydrogen is created. Hydrogen is an extremely flammable gas and can be explosive when mixed with air.
- Powerful oxidants such as hydrogen peroxide can cause fires if they come into contact with organic materials such as wood, paper, cardboard, etc.
- Sulphuric acid mixed with caustic soda creates an important exothermic reaction, which can lead to overflowing or dangerous corrosive projections.

For this reason, the storage of chemical substances requires proper organization, taking into account the hazard of each substance separately as well as the potential reactions between them. The incompatibility rules are presented in chapter 4.4.3, whereas the next table [47] shows most frequently observed dangerous reactions.

Table 4-6: Dangerous reactions

Substance A	+	Substance B	=	Danger
Acids	+	Metals	=	Spontaneous combustion (gaseous hydrogen)
Oxidants	+	Organic substances	=	Fire, explosion
Sulphide	+	Acids	=	Toxic gaseous sulphurated hydrogen
Alkali metals	+	Water	=	Spontaneous combustion (gaseous hydrogen)
Acids	+	Bases	=	Exothermic reaction (heat emission)
Metal powders	+	Aqueous solution	=	Spontaneous combustion (gaseous hydrogen)
Metal powders	+	Air	=	Spontaneous combustion
Nitric acid	+	Organic substances or metals	=	Toxic nitrous gas
Chlorine bleach	+	Acids	=	Toxic gaseous chlorine

4.4.3 Technical solutions

General storage rules

The next chapters present the requirements that must always be met, for the storage of any hazardous material, including the waste generated by the use of these materials.

Marking and labelling

The hazardous substances must be stored in a specific place, room or cupboard, clearly identified and separated from the process areas. The hazard must be indicated and the access restricted.

Every container, from the smallest bottle to the largest tank, must be labelled, in order to provide immediate information on the substance contained and the related hazard. For more information about labelling according to the GHS, refer to Section 4.3.1.

Inventory and safety data sheets (SDS)

In order to have a complete overview of the situation and of the potential hazards in case of an incident (leakage or fire), the company systematically needs to register the stored hazardous substances, including:

- Maximum quantities for every category and updated currently stored quantities
- Storage position(s) on a map

The fire brigade must be informed about the inventory. Furthermore, safety data sheets of every substance must be registered and easily available. Ideally, copies of these SDSs are stored with the substances. They provide information about the hazards, the storage requirements and the expected reactions in case of an accident.

The manufacturers of hazardous materials have to provide safety data sheets with the products they are selling. These SDSs must be regularly updated to comply with national and international standards and requirements. Specific information about SDSs, as specified by the GHS, is provided in Section 4.3.1 in the subsection “GHS safety data sheets”.

Water protection

Every liquid must be stored on a catch basin in order to manage overflow, leakage or accidental spillage. The objective of containing the liquid and avoiding its dispersion is to prevent:

- Environmental contamination and human exposure
- Dangerous reactions

If the substances stored present a high aquatic toxicity, or if this toxicity is low, but the quantities stored are high (over 1,000 kg), the retention capacity must provide for 100% of the highest volume stored plus the retention of the water that would be used to extinguish a fire.

A flow to the sewage system or to surface water must be prevented. The position of evacuation grids must be checked. They might be covered. In case of a dangerous spillage, they must be covered by appropriate means (for example special bags).

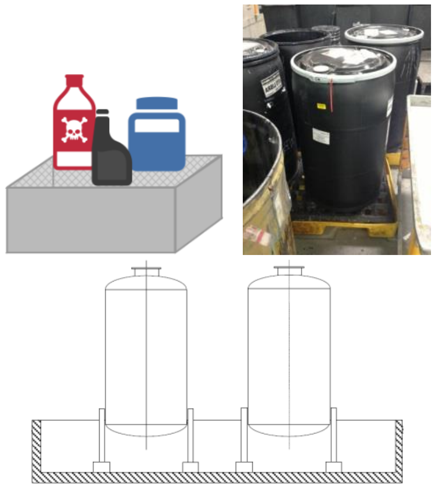


Figure 4-10: Different kinds of catch basins, according to the required volume [74], [1], [53]

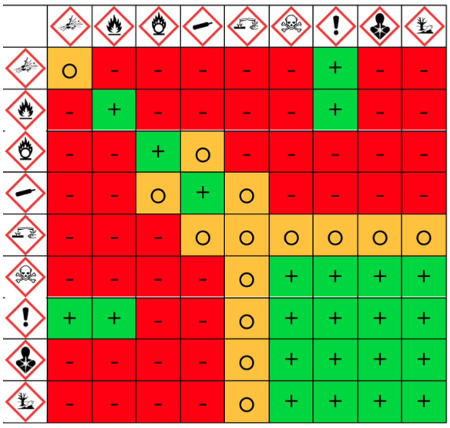
Storage incompatibilities

Hazardous substances must be stored separately from any other non-hazardous material, and especially from food or drugs.

This matrix shows a classification of substances that, according to their hazardous properties, must not be stored together (red), can be stored together under certain conditions that have to be verified in the SDS (orange) or can usually be stored together without disadvantages (green).

Acids and bases must not be stored together.

Appendix 2: Storage shows storage incompatibilities for 16 substances commonly used in industry.



	💥	🔥	⭕	🛢	🧪	☠	!	⚕	🐟
💥	○	-	-	-	-	-	+	-	-
🔥	-	+	-	-	-	-	+	-	-
⭕	-	-	+	○	-	-	-	-	-
🛢	-	-	○	+	○	-	-	-	-
🧪	-	-	-	○	○	○	○	○	○
☠	-	-	-	-	○	+	+	+	+
!	+	+	-	-	○	+	+	+	+
⚕	-	-	-	-	○	+	+	+	+
🐟	-	-	-	-	○	+	+	+	+

Figure 4-11: Storage incompatibilities [based on 55]

Other safety and organizational requirements

- The flooring of the storage area must be impermeable. A special coating (sealing) will often be necessary, as concrete is permeable to many substances. This coating must be incombustible.
- The storage room and the facilities must be made of fire-proof material.
- The separation of the storage areas (or compartments) according to the storage categories must be clearly identified and labelled (flammable, toxic, corrosive, etc.).
- Other non-hazardous materials should not be stored in the same place (wrapping, paper, cardboard, spare parts, etc.).
- A substance must never be stored in a container that is not the original one, unless it has been specifically designed for this use (sufficient mechanic, thermal and chemical resistance).
- The containers must be protected from any mechanical or thermal influence (heat sources, falling objects, pressure through weight, etc.).
- Training must be conducted regarding chemical hazards and behaviour in case of an accident.
- There must be one responsible person (and one deputy) appointed for the storage area(s).

- Appropriate personal protective equipment (PPE) must be easily available and properly maintained.
- At least one eye shower must be installed. An emergency shower can be necessary.

Specific rules for each storage category

Storage category 2: Liquefied gases or gases under pressure

In case of accidental destruction or fire, pressurized containers can turn into dangerous projectiles. Hence, the following safety measures have to be taken:

- Gas bottles must be protected by a fence.
- Use natural or forced ventilation (air renewal 3 to 5 times per hour, extraction near the ceiling or the floor depending on the properties of the gas).
- If the flammable gas is heavier than the air, consider an explosive atmosphere extending from the ground up to 1 metre (Zone Ex 2[17]) [52].
- If the flammable gas is equal in weight or lighter than the air, consider an explosive atmosphere in the whole room (Zone Ex 2).

Figure 4-12: Storage of liquefied gases or gases under pressure [76]

If the vapours or gases are heavier than the air, the openings should be located near the ground. It they are lighter than the air, the openings should be located near the ceiling.

Ammoniac or gaseous chlorine storage requires very specific storage conditions that are not described here.

Storage category 3: Flammable liquids [47], [48]

The vapours of these substances are usually explosive. In exposed rooms, active ignition sources[18] must be avoided. Even the spark of a switch or an electrostatic discharge can set fire to these vapours. Therefore, smoking is strictly forbidden in those areas. In addition, electrical devices must be grounded and used so as to avoid ignition.

Explosive air or gas mixtures are often created in empty containers that have not been cleaned. In a fire situation, flammable substances burn fast or explode. Their flow accelerates the spread of fire.

Flammable liquids are divided into six categories, according to their flashpoint[19].

Figure 4-13: Fire-proof cabinet [76]

F1 = Liquids with a flash point below 21°C

F2 = Liquids with a flash point from 21 to 55°C

F3 = Liquids with a flash point from 55 to 100°C

F4 = Liquids with a flash point above 100°C

F5 = Not easily flammable liquids

F6 = Non-flammable liquids

---

[17] According to ATEX regulations

[18] Active ignition sources include flames, incandescent materials, hot surfaces or sparks emitted electrically, mechanically or electrostatically.

[19] The lowest temperature at which a liquid can vaporize to form a combustible concentration of gas

The storage place shall meet the following requirements, according to the category of the liquid and the quantity stored:

Table 4-7: Storage place depending on the flammable liquid category and the volume (expressed in litres) [based on 48]

Storage place (small container/tank)	Indicative maximum authorized quantity [litres]	
	Categories F1 and F2	Categories F3, F4 and F5
Any type of room	5	30
Cabinet made of materials with low flammability	100	450
Premises with specific structural properties designed to resist fire	> 100	> 450

- For quantities over 100 litres (F1, F2) or 450 litres (F3, F4, F5), the flammable liquid must be stored in a specific room built with material showing specific fire-resistant properties and fire compartments. Consider an explosive atmosphere (Zone Ex 2) extending up to 1 metre above the installation that requires earthing.
- For quantities over 1,000 litres, each substance must be isolated in a specific fire compartment[20]. Consider an explosive atmosphere (Zone Ex 2) extending up to 1 metre above the installation that requires earthing. For quantities over 2,000 litres, protection against lightning is required.

The storage area must be naturally or artificially ventilated:

- Natural ventilation is sufficient if the room is situated above the ground and has two openings directly connected to the ambient air. One of them has to be placed at a maximum of 0.1 metres above the ground. Each opening requires at least 20 square centimetres per square metre of floor area.
- Without sufficient natural ventilation, forced ventilation of the storage area is mandatory (3 to 5 air renewals per hour). The opening has also to be placed at a maximum of 0.1 metres above the ground.
- Storage areas in high-rise warehouses where flammable liquids are stored must be artificially ventilated.

Storage rooms (or racks) must be equipped with drip pans capable of collecting at least the volume of the biggest can, drum or intermediate bulk container (IBC).

Non-buried outdoor storage sites must meet the following requirements:

- Access is limited to authorized persons (a fence is mandatory, surveillance might be needed).
- A safety distance of 5 to 25 metres to neighbouring buildings must be observed, depending on the category, the volume of liquids and the risks for the neighbourhood (see Appendix 2: Storage; [48]).
- An adequately dimensioned drip pan providing for at least the volume of the biggest tank must be installed.

Storage category 4.1: Flammable solid

Dusts can be explosive and therefore dust deposits must be avoided and regularly cleaned.

- For quantities over 1,000 kg, the substances must be isolated in a specific fire compartment.

---

[20] A fire compartment is an area encircled by fire breakers (walls and ceiling must be fire-resistant) in order to prevent fire or smoke from spreading to other areas.

Storage category 4.2: Substances liable to spontaneous combustion (auto-flammable)

These substances can ignite very fast when in contact with the air, even in very low quantities. Examples include phosphor and freshly prepared metallic powders.

- Auto-flammable substances must never be stored outdoors.
- The storage area must be protected from any heat source. Ambient temperature should be controlled.
- They must not be stored with combustive, explosive or flammable substances.
- For quantities over 100 kg, the substance must be isolated in a specific fire compartment.

Storage category 4.3: Substances which, in contact with water, emit flammable gases

The reaction usually releases heat and the gas can ignite spontaneously. Examples include calcium and zinc powder.

- These substances must be stored in a dry place in hermetically closed containers.
- They must not be stored with halogens (fluorine, chlorine, bromine).
- For quantities over 100 kg, the substance must be isolated in a specific fire compartment.
- Specific extinguishers must be available and the sign “Do not extinguish with water” must be visible.

Storage category 5: Oxidizing substances/organic peroxides

These substances form highly flammable or explosive mixtures with any combustible material, flammable substance or just paper, sugar or wood. Notably **organic peroxides** must be carefully stored and handled, as they usually burn explosively.

- These substances must not be stored with combustibles (not even non-hazardous materials such as wood or paper) or caustic substances.
- They can be stored in the same room as other substances, but in a separate specific metal box or cupboard. Some organic peroxides must be refrigerated (well below their decomposition point).
- For quantities over 100 kg, the substance must be isolated in a specific fire compartment.

Storage category 6.1: Toxic substances

Even in very small quantities, these substances can be very harmful, even fatal.

- The storage must be secured and only accessible to authorized persons (key or code).
- For quantities over 1,000 kg, the substance must be isolated in a specific fire compartment.

Storage category 8: Corrosive and caustic substances

These substances can be very harmful, even fatal, in case of contact with the skin, the eyes or in case of ingestion or inhalation of vapours.

- They must not be stored with substances that form toxic gases with acids, or with combustive and oxidizing substances.
- Containers and catch basins must be resistant to corrosion (special plastics).
- Acids and bases must be physically separated and stored on distinct catch basins.
- For quantities over 1,000 kg, the substance must be isolated in a specific fire compartment.
- Storage rooms (or racks) must be equipped with drip pans capable of collecting at least the volume of the biggest can, drum or intermediate bulk container (IBC).

Storage category 9: Miscellaneous dangerous substances and articles, including environmentally hazardous substances

This group includes halogenated hydrocarbons such as perchloroethylene, chloroform or methylene chloride. Concrete is permeable to these highly pollutant substances.

- The catch basin must be capable of collecting at least the volume of 100 per cent of liquids utile volume (real volume occupied by the substance) and not only 100 per cent of the biggest container.
- The storage floor must be coated (sealed).

4.5 Fire protection

Every company should have a fire protection concept. Industries storing or processing any kind of flammable substances are by nature more exposed to the risk of fire, and developing a fire protection concept is therefore mandatory.

This chapter aims primarily at explaining the procedures and working methods for drawing up a fire protection concept and defining associated measures designed to reduce the fire risk.

Fire protection has the following objectives:

- Prevent fire occurrence and fire/smoke propagation
- In case of a fire, ensure effective response
- Provide health protection to persons, rescue teams and animals through safe escape routes
- Protect property (movable and immovable) and the environment

The organization of fire protection must comply with national and regional legislation. As presented in the figure below, it includes the two main aspects fire prevention and rescue procedures.

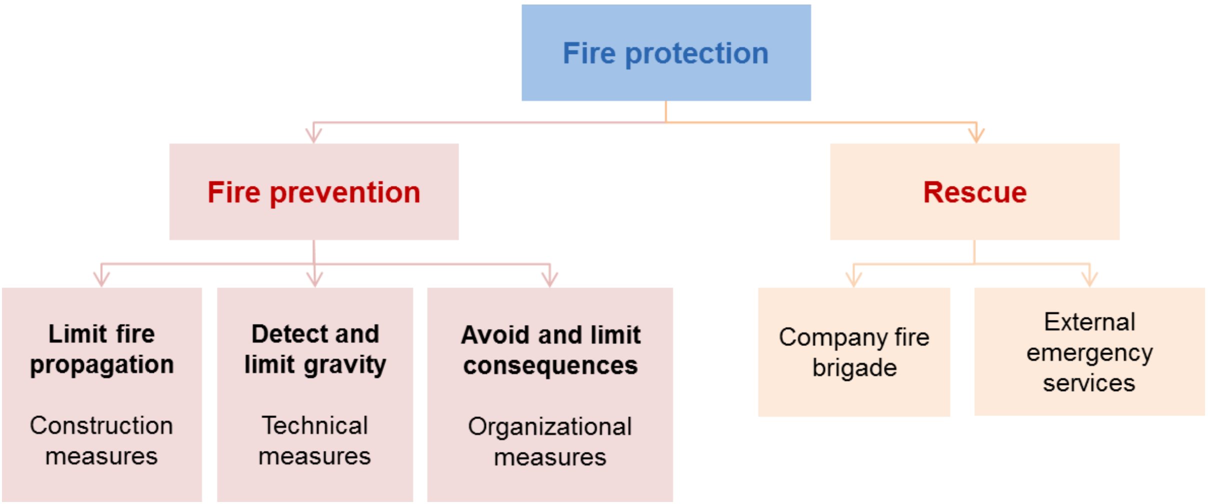


Figure 4-14: Fire protection [74]

Prevention includes structural, technical and organizational measures to limit, detect and avoid the risk of fire. The rescue phase covers support from internal and external emergency services and the fire brigade.

A fire protection concept should include all essential protection measures in terms of construction, technology, processes and organization likely to achieve the objectives of protection.

A fire protection concept is the result of a methodical procedure, as shown in the Figure 4-15, where a range of essential protection measures (structural, technological, process-based, organizational) are planned, taking into account the current situation, the identified hazards and the protection objectives. The concept should ideally be integrated in the planning of new facilities but can as be included in the conversion or restoration of already existing buildings [59].

Figure 4-15: Fire protection concept [74]

4.5.1 Classification/categories

Hazardous materials (hazard inventory)

The Table A4-1 presents the main hazardous material classes affected by fire or explosion hazards, including GHS pictograms and statement codes for different classes of flammable, explosive and oxidizing materials as well as gases under pressure.

The first step of a fire protection concept is to draw up an inventory of flammable, explosive, gaseous and oxidizing materials used in the company in order to define the concerned materials, their quantities and the conditions of storage, handling, processing and disposal.

Fire activation risk (hazard inventory)

The probability of accidentally setting fire to a tank of benzene is higher in a production area (where movements, heat sources or physical dangers are likely to be present) than in a secured storage site. The diagram below shows the increase in probability of the fire activation risk depending on the environmental context and the related physical constraints.

The fire activation risk can be defined as the probability of realization of the risk, depending on the environmental context and related physical constraints. It increases as shown in the diagram below:

- Storage
- Storage + process
- Storage + process + distillation/condensation
- Storage + process + distillation/condensation + pressure (storage and/or process)

The evaluation of the fire activation risk is the basic information to be considered in the fire risk assessment, as shown in Table 4-9. In addition, the following internal and external causes can increase the fire activation risk and might be considered in the risk analysis:

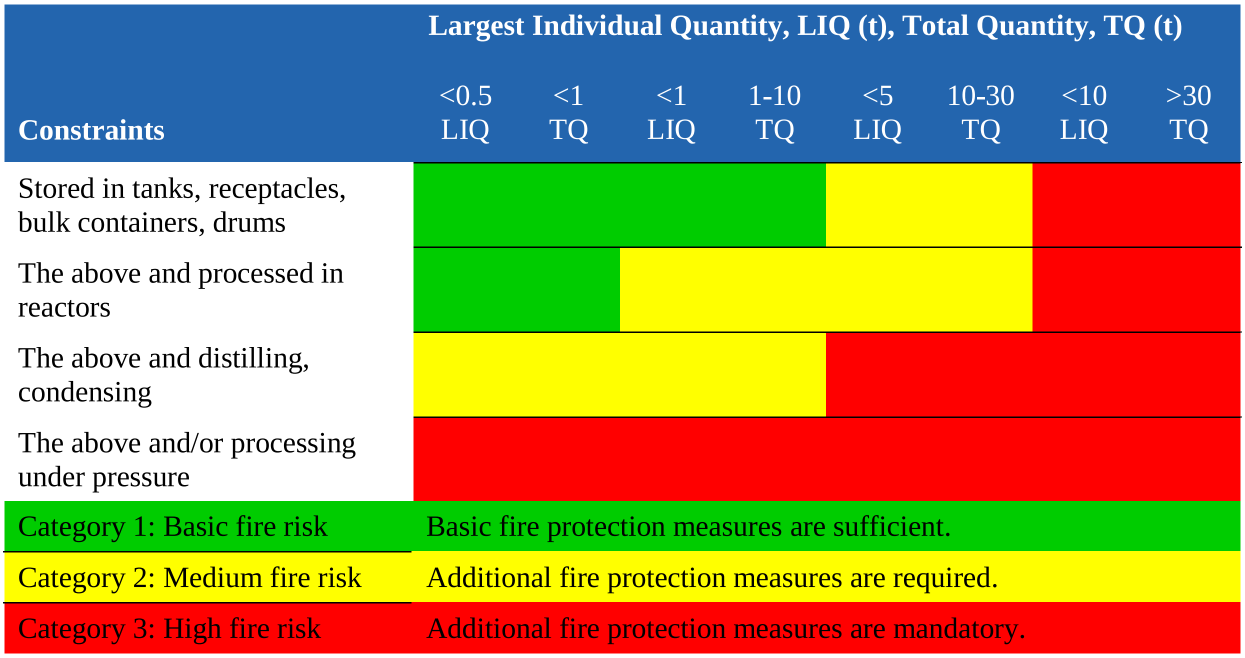
Table 4-8: Internal and external hazards [based on 58]

Internal hazards	**External hazards**
• Ignition sources • Shortage of facilities and missing or damaged fire safety equipment • Lack of organization • Lack of ability to respond to an emergency (lack of training)	• Arson • Natural disasters • Proximity of neighbouring buildings

Fire risk evaluation (risk analysis)

Based on the information collected through the hazard inventory, a rough assessment of the fire risk can be performed, considering the "Largest Individual Quantity" (LIQ) and the "Total Quantity" (TQ) of material identified in the area and the constraints on these materials. The figure below shows how this information can be used for the allocation to one of the three risk categories in order to define the level of protection measures required. The matrix presented here applies to solvents with a boiling point of up to 150°C [56].

Table 4-9: Determination of the fire risk category [based on 56]



	Largest Individual Quantity, LIQ (t), Total Quantity, TQ (t)							
Constraints	<0.5 LIQ	<1 TQ	<1 LIQ	1-10 TQ	<5 LIQ	10-30 TQ	<10 LIQ	>30 TQ
Stored in tanks, receptacles, bulk containers, drums	🟩	🟩	🟩	🟩	🟨	🟨	🟥	🟥
The above and processed in reactors	🟩	🟩	🟨	🟨	🟨	🟨	🟥	🟥
The above and distilling, condensing	🟨	🟨	🟨	🟨	🟥	🟥	🟥	🟥
The above and/or processing under pressure	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
🟩 Category 1: Basic fire risk	Basic fire protection measures are sufficient.							
🟨 Category 2: Medium fire risk	Additional fire protection measures are required.							
🟥 Category 3: High fire risk	Additional fire protection measures are mandatory.							

In order to define specific measures, the fire risk should be assessed separately for each area.

4.5.2 Technical solutions (risk reduction measures)

Based on the categories defined by the risk analysis, appropriate measures can be taken in relation to construction, technology and organization in order to reduce the fire risk.

The following sections are inspired by the CFPA Guidelines "Fire protection on chemical manufacturing sites" [56] and "Safety distances between waste containers and buildings" [57].

Construction measures

The global purpose of applying structural measures is to limit fire propagation. These measures prevent the propagation of a fire by using suitable construction materials and confine the fire through fire compartments.

Table 4-10: Fire protection – Construction measures (non-exhaustive list) [based on 56]

Construction measures	**Fire risk**		
	Basic	Medium	High
Maintain safety distances to other buildings (2.5 metres), especially for premises where hazardous products are stored.	X	X	X
Use non-combustible building materials, especially for supporting structures and exterior walls.	X	X	X
Separate different types of activities in separate fire-compartments (administration, storage, production).	X	X	X
Limit the size of the fire compartments, especially of those with a high fire hazard.	X	X	X
Adapt the fire resistance of the compartments to the amount of flammable/explosive products and the fire activation risk.	X	X	X
Provide enough safe escape routes.	X	X	X
Install drainage and spill control systems designed to contain leakages and firefighting water.	X	X	X

In addition, the following information should be observed:

- The minimum horizontal safety distance between combustible objects and buildings is 2.5 metres. Certain situations require a larger safety distance (4, 6 or 8 metres) depending on the content, number and volume of the containers. Other parameters can affect this safety distance. Interested readers can find more detailed information in the corresponding guideline published by CFPA Europe [57].
- Buildings where flammable products are stored and handled must be made of non-combustible materials, including the insulation in roofs and walls. Floors of multi-level buildings, open structures and load-bearing structures should preferably be made of concrete.
- The maximum size of a fire compartment is about 3,200 square metres.
- The drainage and spill control systems must be designed for simultaneous flow of flammable liquids and fire-fighting water away from the building.
- It is essential that there is enough retention capacity for the firefighting water, especially if the products stored are dangerous to the aquatic environment or the soil.

Technical measures

Technical measures are implemented to detect the fire risk by using alarms and fire or gas detection devices, and to limit the impact by using water, fire extinguishers or a sprinkler system. Specific installations and devices are needed to protect an object from fire risk [56].

Table 4-11: Fire protection – Technical measures (non-exhaustive list) [based on 56]

Technical measures	Fire risk		
	Basic	Medium	High
Provide air handling and smoke exhausting systems (automatic + manual)	X	X	X
Provide manual firefighting equipment in adequate quantity (internal fire hydrants, fire extinguishers, etc.)	X	X	X
Provide manual alarm points	X	X	X
Provide an automatic fire detection system		X	X
Provide an automatic fire extinction system (with adequate extinguishing agents)			X
Provide a gas detection system			X
Install a lightning rod for all production buildings with significant amounts of flammable or explosive products	X	X	X
Install a safety lighting system	X	X	X
Provide sufficient fire water capacity	X	X	X

Furthermore, the following items have to be considered:

- The maximum distance between internal fire hydrants should be around 75 metres.
- Manual fire alarm points must be strategically located throughout the site and production units. Alarm points need to be provided at 60 metre intervals.
- Fire detection systems are mandatory in areas with low manning levels (automated plants). The system has to be strategically positioned in order to detect fires starting inside processing equipment.

Figure 4-16: Fire alarm [74]

- Gas detection systems should be provided where potential leak sources could occur (pumps, compressors, tank cars, control rooms, etc.) in order to be used for emergency functions like shutdown of processes and/or activation of emergency ventilation.
- According to evaluations of firefighting statistics, fire water volumes of 8,000 l/min up to 12,000 l/min are required without fixed extinguishing systems. The water supply should provide fire water for a minimum of two hours and preferably 3 to 4 hours. The water retention capacity must be designed accordingly.

Figure 4-17: Gas detector [74]

Organizational measures

Organizational measures are implemented to avoid and control the impact of a fire and include the training of employees, the maintenance of equipment and the provision of safe escape routes.

Table 4-12: Fire protection – Organizational measures (non-exhaustive list) [based on 56]

Organizational measures	**Fire risk**		
	Basic	**Medium**	**High**
Establish a preventive maintenance programme for all equipment, including fire protection equipment	X	X	X
Appoint an adequately trained person responsible for fire protection	X	X	X
Organize an employee training programme		X	X
Organize a training programme for visitors			X
Develop an escape and emergency plan		X	X
Organize evacuation exercises with local emergency services		X	X

Responsibilities include the coordination and implementation of the fire protection measures, focusing in particular on the following points:

- An internal inspection system should be implemented to ensure the periodical checks of installations and organizational measures that are relevant to fire protection.
- A person responsible for fire protection must be appointed and given practical training.
- All employees must receive periodical training on fire safety and emergency procedures.
- The fire protection documentation such as escape and emergency plans has to be continually updated and made available in every building in case of an emergency. An example is provided in Appendix 3: Fire protection)

4.6 Management of chemical waste

Out of 5 to 7 million known chemical substances, more than 80,000 are used by companies in their production processes and operations. Numerous new chemicals are developed and produced every year. Today, almost every company uses some type of chemicals and generates chemical waste. Those enterprises which effectively manage chemicals and chemical waste can gain concrete benefits.

In general, hazardous waste is any waste or combination of waste which may have detrimental effects on the environment or human health because of its specific nature. These wastes not only pose risks and hazards because of their nature but also have the potential to contaminate large quantities of otherwise non-hazardous wastes if allowed to mix. [44, p. 9]

Benefit by reducing costs and environmental impact

Chemicals can represent a major part of the production cost for companies. Any measures that can be taken to reduce the loss, waste, contamination and expiry of these substances will bring cost savings to companies and, at the same time, reduce their environmental impact.

Benefit by becoming more competitive

By improving the management of chemicals and chemical waste, companies that are striving to achieve certification under management system standards such as ISO 9000 (quality) and 14000 (environment) will gain synergies. Many of the activities required for Environmental Management Systems (EMS) certification are aimed at reducing the use of hazardous substances, protecting the health of workers and reducing negative effects on the environment.

Benefit by improving workers health and safety

Reducing health and safety risks for employees improves their motivation and productivity and reduces absenteeism due to injury and illness.

4.6.1 Waste management options

In Europe, waste producers have a statutory duty to consider the **waste hierarchy** when deciding how to deal with waste.

Hazardous waste hierarchy

The waste hierarchy is a concept at European level that provides a preferred order of priorities for selecting, ranking and deciding upon waste management options with the aim to conserve resources and to minimize environmental damage. It gives top priority to preventing waste in the first place. When waste is created, it gives priority to preparing it for re-use, then recycling, then recovery, and last of all disposal (for example landfill).

In the European Union Waste Framework Directive (2008), the waste hierarchy has five steps: prevention, preparing for re-use, recycling, other recovery (for example energy recovery) and disposal. [61, p. 3]

Prevention means measures taken before a substance, material or product has become waste in order to reduce:

- The quantity of waste, also through the re-use of products or the extension of the life span of products
- The adverse impacts of the generated waste on the environment and human health
- The content of harmful substances in materials and products

Re-use means any operation by which products or components that are not waste are used again for the same purpose for which they were conceived.

Preparing for re-use means checking, cleaning or repairing operations, by which products or components of products that have become waste are prepared so that they can be re-used without any other pre-processing.

Recycling means any recovery operation by which waste materials are reprocessed into products, materials or substances, whether for the original or other purposes. It includes the reprocessing of organic material but not energy recovery or the reprocessing into materials that are to be used as fuels or for backfilling operations.

Recovery means any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy.

Disposal means any operation which is not recovery even where the operation has a secondary consequence, the reclamation of substances or energy.

Other recovery is not specifically defined in the revised Waste Framework Directive, although ‘energy recovery’ is referenced as an example. Since the term ‘other recovery’ is explicitly excluded from the definition of recycling, ‘other recovery” can be considered the processing of wastes into materials to be used as fuels or for backfilling.

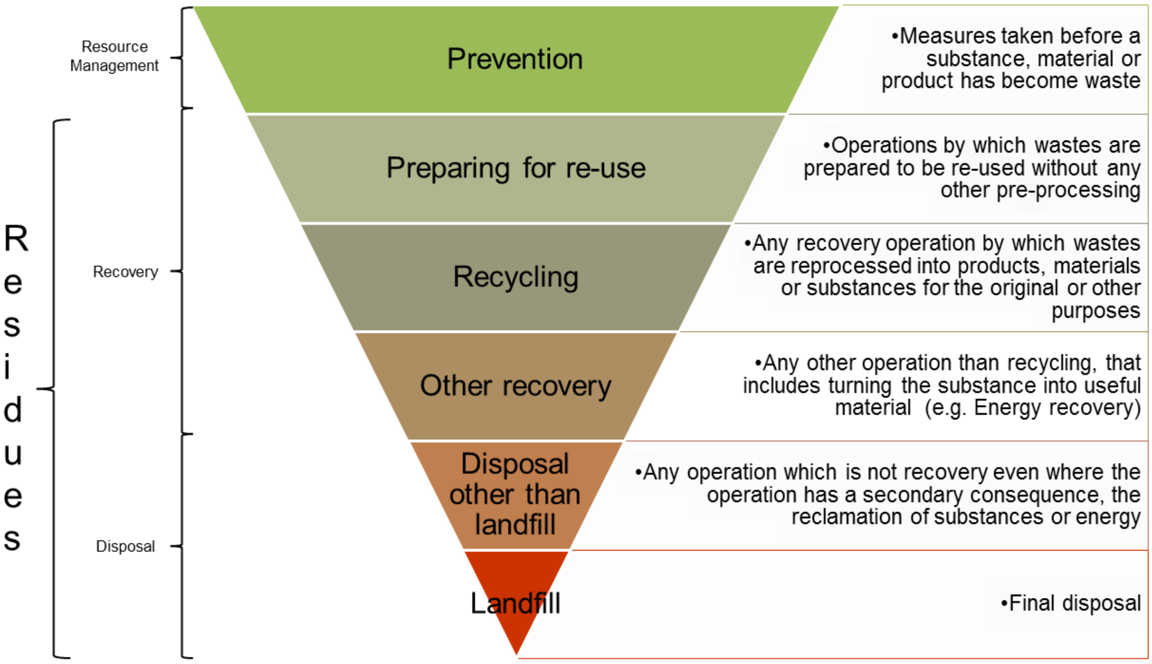


Figure 4-18: Hazardous waste hierarchy [based on 77]

4.6.2 Good practices in hazardous waste management

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal defines the **environmentally sound management of hazardous wastes** as “taking all practicable steps to ensure that hazardous wastes or other wastes are managed in a manner which will protect human health and the environment against the adverse effects which may result from such wastes” [65, p. 17].

Therefore an overarching objective of the sound management of hazardous waste is to minimize the negative effects of the generation and management of hazardous waste on human health and the environment.

A very useful flow diagram to start a hazardous waste management plan, is shown in the document “Guidance on applying the waste hierarchy to hazardous waste” by DEFRA [77, p. 15].

Handling of hazardous waste

Adequate handling of hazardous waste is an integral part of the waste management system. The list below provides an overview of good management practices that help avoiding accidents:

- Train personnel on safe procedures to transfer chemicals to waste containers.
- Ensure that waste containers are in good condition.
- Check whether waste containers are compatible with the waste type they are expected to contain.
- Keep an adequate spill control kit nearby. The kit should be big enough to control the release of the largest type of container in the storage area. Clean up spills quickly.
- When handling waste containers, use mechanical aids such as drum lifts, drum hand trucks and drum dollies. Do not roll drums on their side or edge.
- Make sure container caps are secure.
- Train personnel on spill clean-up procedures.
- Maintain good general housekeeping. Keep aisles and walkways clear [78].

Identification, classification and labelling of hazardous waste

The hazardous waste identification and classification process is the crucial first step in the hazardous waste management system.

Identification and classification

The waste producers usually possess the best knowledge of the generated waste, as they are aware of the raw materials[21] used in the production process and the technologies applied. They should be in charge of the proper classification and registration of their waste. If already available, the national classification system should be used. In any case, a basic characterization with the indication of the main physical and chemical properties is necessary. Further information on other hazardous properties such as explosivity, corrosivity, etc. should be provided. If possible, indications for the appropriate waste treatment could already be given (for example methods of stabilization) [62, p. 234].

Two of the main systems for hazardous waste identification are that of the European Union (EU) and that of the US Environmental Protection Agency (US EPA). These systems determine whether a waste is recognized as hazardous or non-hazardous and are based on defining threshold concentrations for the hazardous characteristics. If the waste exhibits hazardous characteristics at a quantity above such thresholds, it is then considered to be hazardous [63, p. 9].

Labelling

As a generator of hazardous waste, you are responsible for assuring that any container used to accumulate hazardous waste is properly labelled in order to meet regulatory requirements and assure the safety of those around you. During storage and transport, it is important that your waste can be easily identified and that containers are labelled with the following information:

- Indication that it is waste
- Contents of the container (where it is a chemical you should use the chemical identity rather than a trade name)
- Data of the waste generator
- State of the substance (solid, liquid or gas)
- Hazard(s) where applicable
- Emergency contact details [64, p. 4]

Hazardous waste management components

In principle, waste management comprises any step of handling waste from the moment of its generation up to the moment of its final disposal or its re-entering into the product status by means of recycling or recovery. Accordingly, the EU Waste Framework Directive defines waste management as “the collection, transport, recovery and disposal of waste, including the supervision of such operations and the after-care of disposal sites, and including actions taken as a dealer or broker”.

Segregation

It is important that hazardous waste is segregated properly because of the effects it may have on human health or the environment if it is not properly controlled.

You must keep separate:

- Hazardous waste from non-hazardous waste
- Different types of hazardous waste from each other, and
- Hazardous waste from other materials [64, p. 3].

---

[21] Safety data sheets (SDSs) are an important information source to determine whether the waste you produce is hazardous.

Storage

Hazardous waste should be properly stored on-site. The storage areas should be away from public places in order to prevent any harm to the public or those persons exposed to the waste, and should be adequately dimensioned for the waste quantities to be stored.

The key factors which a company needs to ensure are that waste is:

- Secure
- Contained so that it cannot escape
- Protected from the weather, vehicles (including fork lift trucks), and scavengers and pests [64, p. 4].

It is important to ensure that any container used for waste meets certain minimum requirements. First and foremost, the container and its closure need to be compatible with the contained waste.

For certain wastes, there are additional storage requirements, for example chemicals which can have different properties and have the potential to react dangerously if not properly stored. The Health and Safety Executive, UK, have produced guidance on dealing with chemical storage (HSG 71)[22] and the storage of flammable chemicals (HSG 51)[23].

In small and medium enterprises, often only small quantities of hazardous wastes are generated. Therefore, on-site collection and temporary storage is necessary until quantities are large enough for shipment by a licensed hazardous waste transporter.

Hazardous waste should be stored so as to prevent or control accidental releases to air, soil and water resources in a location where [79, p. 48-49]:

- Waste is stored in a manner that prevents the commingling or contact between incompatible wastes, and allows for inspection between containers to monitor leaks or spills. Examples include sufficient space between incompatibles or physical separation such as walls or containment curbs.
- Waste is stored in closed containers away from direct sunlight, wind and rain.
- Secondary containment systems should be constructed with materials appropriate for the wastes being contained and adequate to prevent loss to the environment.
- Secondary containment is included wherever liquid wastes are stored in volumes greater than 220 litres. The available volume of secondary containment should be at least 110 per cent of the largest storage container, or 25 per cent of the total storage capacity (whichever is greater), in that specific location.
- Adequate ventilation is provided where volatile wastes are stored.

Hazardous waste storage activities should also be subject to special management actions, conducted by employees who have received specific training in handling and storage of hazardous wastes. These activities include [79, p. 49]:

- Providing readily available information on chemical compatibility to employees, including labelling each container to identify its contents
- Limiting access to hazardous waste storage areas to employees who have received proper training
- Clearly identifying (label) and demarcating the area, including documentation of its location on a facility map or site plan
- Conducting periodic inspections of waste storage areas and documenting the findings
- Preparing and implementing spill response and emergency plans to address their accidental release
- Avoiding underground storage tanks and underground piping of hazardous waste

---

[22] Health and Safety Executive, 2009. Chemical warehousing: The storage of packaged dangerous substances. HSG 71

[23] Health and Safety Executive, 1998. The storage of flammable liquids in containers. HSG 51

Collection and transportation

On-site and off-site transportation of waste should be conducted so as to prevent or minimize spills, releases and exposures of employees and the public. A licensed waste transporter[24] must ensure that hazardous waste is packaged, documented and labelled in compliance with the method of transport used (road, rail, air or sea) [65, p. 49].

Moreover, the transporter must ensure that the emergency response information contained on the manifest is immediately accessible to emergency responders. The transporter regulations do not apply to the on-site transportation of hazardous waste by generators who have their own treatment or disposal facilities, nor to TSD facilities transporting wastes within a facility.

All waste containers designated for off-site shipment should be secured and labelled with the contents and associated hazards, properly loaded on the transport vehicles before leaving the site, and accompanied by a shipping paper (i.e., EU consignment note [25] or US hazardous waste manifest[26]) that describes the load and its associated hazards [79, p. 49]). Completion of the documentation together with proper marking and labelling of containers and vehicles enables police, ambulance, fire and other first responders to react effectively and safely in the event of a spill or other accident involving hazardous waste while in transit.

Information required for consignment notes in the UK including an example can be found in the Guide to Hazardous Waste Regulations for small businesses published by the UK Environment Agency [64, p. 6]. However, local regulations and requirements must be observed.

Treatment and disposal of hazardous wastes

The purpose of treating hazardous waste is to convert it into non-hazardous substances or to stabilize or encapsulate the waste so that it will not migrate and present a hazard when released to the environment. Treatment methods can be generally classified as chemical, physical, thermal and/or biological.

Some types of waste may be managed properly and legally at company premises (for example in case of reuse). Other types require particular handling and shipment to businesses that are specialized and licensed in storage, recycling, treatment and disposal technologies. It is the responsibility of an enterprise to decide which method of management is best for the facility in terms of future liability, potential adverse environmental impact and cost [79, p. 48].

Selected management approaches should be consistent with the characteristics of the waste and local regulations, and may include one or more of the following [79, p. 48]:

- On-site or off-site biological, chemical or physical treatment of the waste material to render it non-hazardous prior to final disposal
- Treatment or disposal at authorized facilities specially designed to receive the waste. Examples include composting operations for organic non-hazardous wastes, properly designed, licensed and operated landfills or incinerators designed for the respective type of waste, or other methods known to be effective in the safe, final disposal of waste materials such as bioremediation.

In the absence of qualified commercial or government-owned waste disposal operators (taking into consideration proximity and transportation requirements), companies should consider [79, p. 50]:

- Installing on-site waste treatment or recycling processes

---

[24] US EPA regulations governing hazardous waste transporters: http://www.epa.gov/osw/inforesources/pubs/orientat/rom34.pdf

EU DIRECTIVE 2008/68/EC on the inland transport of dangerous goods:
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:260:0013:0059:en:PDF

[25] EC detailed description of consignment note data: http://ec.europa.eu/transport/rail/interoperability/doc/aeif-annex-a3-en.pdf

[26] US EPA hazardous waste manifest system: http://www.epa.gov/waste/hazard/transportation/manifest/index.htm

- As a final option, constructing facilities that will provide for the environmentally sound, long-term storage of wastes on-site or at an alternative appropriate location until external commercial options become available

The following table shows the main processes for waste treatment and disposal:

Table 4-13: Waste disposal technologies [based on 80, p. 147]

1. Physical treatment processes			2. Chemical treatment processes	3. Biological treatment processes	4. Thermal treatment processes	5. Disposal processes
a. Gas cleaning	**b. Liquids-solids separation**	**c. Removal of specific components**	**a. Absorption**	**a. Aerobic systems**	**a. Incineration**	**a. Deep-well disposal**
i. Mechanical collection	i. Centrifugation	i. Adsorption	**b. Chemical oxidation**	**b. Anaerobic systems**	**b. Pyrolysis**	**b. Dilution and dispersal**
ii. Electrostatic precipitation	ii. Clarification	ii. Crystallization	**c. Chemical precipitation**	**c. Activated sludge**	**c. Vitrification**	**c. Ocean dumping**
iii. Fabric filter	iii. Coagulation	iii. Dialysis	**d. Chemical reduction**	**d. Spray irrigation**		**d. Sanitary landfill**
iv. Wet scrubbing	iv. Filtration	iv. Distillation	**e. Wet oxidation**	**e. Tricking filters**		**e. Land burial**
v. Activated carbon adsorption	v. Flocculation	v. Electrodialysis	**f. Ion exchange**	**f. Waste stabilization ponds**		
vi. Adsorption	vi. Flotation	vi. Evaporation	**g. Neutralization**	**g. Rotating bio contactors**		
	vii. Foaming	vii. Leaching	**h. Chemical fixation and solidification**			
	viii. Sedimentation	viii. Reverse osmosis	**i. Dehalogenation**			
	ix. Thickening	ix. Solvent extraction				
		x. Stripping				

Monitoring

Monitoring activities associated with the management of hazardous and non-hazardous waste should include:

- Regular visual inspection of all waste storage and collection areas for evidence of accidental releases and verification that wastes are properly labelled and stored. When significant quantities of hazardous wastes are generated and stored on site, monitoring activities should include:
    - Inspection of vessels for leaks, drips or other indications of loss
    - Identification of cracks, corrosion or damage to tanks, protective equipment or floors
    - Verification of locks, emergency valves and other safety devices for easy operation (lubricating if required and keeping locks and safety equipment in standby position when the area is not occupied)
    - Checking the operability of emergency systems
    - Documenting results of testing for integrity, emissions or monitoring stations (air, soil vapour or groundwater)
    - Documenting any changes to the storage facility and any significant changes in the quantity of materials in storage
- Regular audits of waste segregation and collection practices including tracking of waste generation trends by type and amount of waste generated, preferably by facility departments
- Characterizing waste at the beginning of the generation of a new waste stream, and periodically documenting the characteristics and proper management of the waste, especially hazardous wastes
- Keeping manifests or other records that document the amount of waste generated and its destination
- Periodic auditing of third-party treatment and disposal services including re-use and recycling facilities when significant quantities of hazardous wastes are managed by third parties. Whenever possible, audits should include site visits to the treatment storage and disposal location.

4.6.3 Additional sources of information

Websites

UNEP-Global Partnership on Waste Management (**GPWM**): provides a guideline platform that deals with different aspects of waste management, including hazardous waste: http://www.unep.org/gpwm/InformationPlatform/WasteManagementGuidelines/tabid/104478/Default.aspx

UK Environment Agency: provides information and guidelines that will help you classify your waste (using the List of Waste), identify if it is hazardous waste, and understand the controls that apply to hazardous waste: http://www.environment-agency.gov.uk/business/topics/waste/32180.aspx

Website of the **European Commission**: provides information on EU hazardous waste legislation: http://ec.europa.eu/environment/waste/hazardous_index.htm

Documents

DEFRA (Department for the Environment, Food and Rural Affairs, UK):“Guidance on Applying the Waste Hierarchy to Hazardous Waste” (2011). This guidance is for any business or public body which generates, handles or treats hazardous waste.

GIZ (Deutsche Gesellschaft für Internationale Zusammenarbeit) “Manual on industrial hazardous waste management for authorities in low and middle income economies” (2012): gives an overview of key issues related to legal requirements and practical procedures pertaining to the environmentally sound management of hazardous waste, taking into account requirements, recommendations and guidelines supplied by the Basel Convention and OECD, where relevant, and providing provisions and procedures, in particular from the European Union, as model examples.

IFC (International Finance Corporation, World Bank Group): "General EHS Guidelines: Environmental Waste Management" (2007): provides general guidelines for the management of non-hazardous and hazardous waste

EU: "Reference Document on Best Available Techniques for the Waste Treatments Industries" (2006): provides BAT in the waste treatment sector, including generic BAT and BAT for specific types of waste treatments

Environment Agency UK: "Guide to the Hazardous Waste Regulations for Small Businesses" (2013): explains how to determine if your waste is hazardous and what your responsibilities are as a producer of hazardous waste

Blackman, William C. "Basic hazardous waste management", third edition (2001), Lewis Publishers, CRC Press LLC.

4.7 Energy efficiency and chemicals

Industrial boiler design and operating conditions can have a significant impact on the production of persistent organic pollutants (POPs). Boilers are used for heating water for industrial processing or for domestic and industrial heating but also for producing steam. They can unintentionally form or release dioxins and furans (PCDD/F) or hexachlorobenzene (HCB). It has been demonstrated that it is possible for these compounds to be unintentionally formed during the combustion of fossil fuels. The volumetric concentrations of these pollutants in the emissions from boilers are generally very low. However, the total mass emissions from the boiler sector may be significant because of the scale of fossil fuel combustion in terms of tonnage and distribution. Besides the emission of POPs, the combustion of fossil fuels also forms other types of pollutants like SO_2, NOx, CO and particulate matter that may have a significant effect on the environment [67].

The unintentional production of POPs compounds during the combustion process follows three general pathways:

- Undestroyed compounds originally present in the fuel
- Gas-phase formation from precursors (for example polyhalogenated phenols, chlorinated aromatic compounds) at temperatures higher than 500°C
- Re-formation of POPs in the cooling of flue gases

Modern industrial boilers are normally identified by the methods of heat transfer utilized.

4.7.1 Heat transfer systems

- Water-tube boilers: Heat transfer tubes containing water are directly contacted by hot combustion gases. Commonly used in coal fired boilers but can accommodate almost any combustible fuel including oil, gas, biomass and refuse-derived fuel (RDF).
- Fire-tube boilers: Water surrounds tubes through which hot combustion gases are circulated. The application is more common for pulverized coal, gas and oil fired boilers but various types can also burn biomass and RDF. They are generally used for lower pressure applications.
- Cast-iron boilers: Cast sections of the boiler contain passages for both water and combustion gas, used for low-pressure steam and hot water production. They are generally oil or gas fired with a smaller number of coal-fired units.

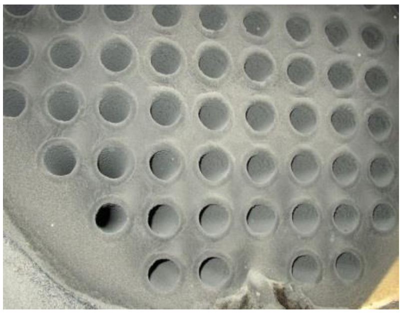


Figure 4-19: Fire-tube boiler (opened) [74]

4.7.2 Fuel type

Various types of fuels such as coal, oil, gas and biomass are used either individually or in combination with energy-containing waste products from other processes for steam and hot water generation in boilers. The type of fuel used depends on fuel availability and process economics.

Heavy fuel oil is still combusted for steam generation and is usually burned in specially designed burners incorporated in the boiler walls. The formation of PCDD/PCDF is favoured during co-combustion when liquid or sludge wastes such as waste oil or used solvents are added to the fuel mix, possibly due to lowered combustion efficiency.

Figure 4-20: Fuel oil operated boilers [74]

Light fuel oil and natural gas are always fired in specially designed burners and are generally unlikely to generate large amounts of PCDD/PCDFs, since both are very high calorific, clean-burning fuels with little ash.

Coal use in less efficient sectors could be a significant source of local emissions. It is acknowledged that the reduction techniques for dusts, SO2 and NOx on a flue gas can also reduce or remove PCDD/PCDF. This reduction is inconstant.

The use of **biomass** energy derived from renewable animal and plant sources can contribute to the energy requirements of industrial boilers. Usually the combustion of renewable biomass is less efficient than conventional fossil fuels and it is mostly burnt as a supplement along with feed from a conventional fossil fuel energy source. Potential for POPs emission may be increased by co-firing biomass if the boiler efficiency is not maintained by appropriate system redesign or control.

4.7.3 Emission reduction measures

In order to reduce the emission of POPs from fossil fuel-fired industrial boilers, the three pathways mentioned above must be minimized in the design and operation of the process. This will be effectively achieved by addressing:

- Energy conservation
- Fuel quality
- Combustion conditions
- Installation of most appropriate air pollution control devices

While the low level of precursors necessary to promote the unintentional formation of POPs via gas formation above 500°C occurs in most fuels, attention must be paid to reduce, as much as possible, the unintentional introduction of contaminated fuels, which may promote the formation of POPs. This is especially valid when co-firing fossil fuels with waste material. Other types of pollutants like SO_2 can also excessively occur due to low fuel quality.

The table below shows the scale of the potential firing technique savings achieved by the designated remedial actions. This is only a rough calculation. The actual savings would have to be calculated based on the actual plant and using the current operating profile. The designated values depend on the plant’s condition.

Table 4-14: Energy saving potential in different areas of an industrial combustion plant

Loss	Remedy	Energy savings
Flue gas losses	Economizer Air pre-heater Condensing technology	3-15%
Surface losses	Appropriate insulation Lower boiler pressure Combustion air from top of boiler house	0.3-1%
Purging losses	Optimize control circuits Hot standby Set wider turndown ratio of burner	0.2-5%
Boiler scale	Correct feedwater preparation Clean boiler Optimize flue gas temperature	Up to 10%
Water losses	Replace pipes Renew seals Change valves and cocks	0.2-1%
Blowdown losses	Retrofit continuously regulated blowdown Fit blowdown heat exchanger Correctly adjust blowdown valve	0.5-5%
Excess air	Retrofit electronic compound regulator Retrofit O_2 and CO control system	0.5-1.5%
Plumes of steam	Retrofit vent condenser Retrofit deaerator control unit Retrofit magnetic shut-off valve	0.3-4%

Combustion conditions

To achieve the complete combustion of POPs contained in the fuel, special attention has to be paid to the four cornerstones of high destruction efficiency: **temperature**, **time**, **turbulence** and **excess oxygen**. In this way, precursors are destroyed and soot formation is reduced, allowing fewer possible sites for solid catalysis in the cooling gas effluent. It is generally accepted that a temperature over 900°C and a gas residence time of 2 seconds are sufficient to achieve the complete oxidation of dioxins as long as the gas flow is sufficiently turbulent and excess oxygen is present.

The air-fuel ratio for every firing has to be precisely calculated and adjusted accordingly to obtain the required output. Each level of output or quantity of fuel requires an exact amount of air. A regulator is required to calculate how much air is needed for which quantity of oil and gas. Mechanical regulators are robust, easy to use and have an air curve for all fuels but the mechanical tolerance could result in excess amounts of air being used and might not compensate temperature variations [68].

With electronic compound regulation, a microcontroller adjusts all firing functions individually. For this purpose, each valve and trap has its own actuator which is individually programmed at each load point. This means that different programmes can be used for different fuels. By using precisely adjusted valves and traps, the fuel consumption can be drastically reduced, whilst allowing O_2 and CO regulation.

The different densities of the hot and cold induction air have an effect on the oxygen transfer and may change fuel consumption significantly. Fixed regulation means that a burner set up in winter with little excess air may be operated in summer with an air deficit if the supply is not manually adjusted. A combined O_2/CO regulation always prevents an excess of air within a defined, lower range and equalizes the constant variations between temperature and pressure in the ambient air. It includes a broad regulation range for the O_2 content. In addition, CO occurs as a stop signal. Gases are measured by a lambda wave in the waste gas stream and the measurement signals are used to regulate the amount of air. A lower quantity of excess O_2 therefore results in fuel savings of up to 2 per cent.

Heat recovery

Usually, the waste gas temperature is slightly above the medium temperature when heat is generated at 30-50 K, which represents the lowest threshold at which the waste gas can be cooled inside the boiler. Waste gas temperatures of 250° C or even 400° C downstream of thermal oil heaters therefore occur inside the plant. The residual heat contained in the exhaust gas can be partially recovered through heat exchange by using so-called economizers that preheat the feed water, or through air-to-air heat exchangers that heat the fresh air. Regardless of the type of heat exchanger, a retrofit achieves significant savings if the plant discharges large quantities of waste gas. As a rule of thumb, a 100 K reduction of the waste gas temperature saves 4 per cent of fuel, whatever the operating method.

An **economizer** passes boiler feed water through the waste gas stream at a temperature of 103° C, before it returns to the boiler, causing the temperature to increase from 125° C to 135° C while the waste gas is cooled down. This temperature should not be exceeded in order to avoid the condensation of the waste gas in the chimney, which may cause construction damage or corrosion. If the sulphur concentration in the waste gas is elevated, the temperature must be even higher. In addition, if the waste gases contain dust, the heat exchanger’s geometry will have to be adjusted to prevent blockage. Using an economizer has been tested worldwide and it works: the higher the waste gas temperature the longer the full-load operation and the quicker the amortization.

Economizers must not be used, if the boiler contains high-pressure condensates or if thermal oil is used instead of water. In this case, **air-to-air heat exchangers (air pre-heaters)** are used. This type of heat exchanger uses the residual energy of the waste gas to heat the burner’s combustion air and can reduce energy costs by over 5 per cent. Usually, however, the burner control has to be reconfigured, if the fuel-air ratio is altered.

If the waste gas is cooled again downstream of the economizer, condensate is formed. In this case, the so-called **condensing technology** can be used to recover condensation heat. It involves a heat exchanger in the waste gas with sufficiently cold surfaces, on which water vapour can condense. The heat exchanger must be made of stainless steel and is connected to a condensate removal system in order to avoid corrosion by the acidic condensate. The waste gas is cooled down to a temperature of 45 to 50°C and fresh water can be heated to approximately 60°C. A 50-per cent condensation of the waste gas may result in 5.5 per cent fuel savings.

Depending on the heat generator, it is also possible to combine all three heat recovery technologies, specifically economizers, condensing technology and air pre-heaters. The table below summarizes the potential energy savings achieved by these three technologies.

Table 4-15: Potential energy savings of different heat recovery technologies

Technology	Medium	Operational area	Potential saving
Economizer	Waste gases/water Boiler supply water pre-heated	Downstream of heat exchanger; for supply water	4-7%
Air-to-air heat exchanger	Waste gas/air Combustion air pre-heated	Downstream of heat exchanger at high temperatures (water tube boilers, thermal oil heaters) or residual heat final phase	4-10% (water tube boilers, thermal oil heater) 0.5-4% (final phase)
Condensing technology	Waste gas/water Prepared water/process water pre-heated	As second heat exchanger downstream of an economizer or air-to-air heat exchanger	4-7%

Blowdown

When vapour is removed from the boiler, salts are concentrated as water is continually added to the boiler. The amount of salt and additives depends greatly on the way the water was previously processed and is lowest in de-ionized supply water. The dissolved salts, particularly sodium hydrogen carbonate, are expelled from the boiler using the blowdown valve, with hot water being discharged along with the accumulated salt. The manual operation of the blowdown valve often results in unwanted water and energy losses, since the salt concentration is not always visible in the water. By continuously measuring the electrical conductance, an undesired high carbonate content of the water can be determined. Coupled with a regulator and an automatic blowdown valve, the conductance, and therefore the salt content in the boiler water, may be kept exactly below a set threshold level and no more water than necessary is discharged.

Using a blowdown cooler, the residual water may then serve to heat up additional water, which then flows from the water processor into the degasser.

These measures discharge cool salt water while heat and expensive supply water remain in circulation and can achieve energy savings of up to 5 per cent.

5 Supporting policies

The implementation of innovative solutions for the sound management of chemicals and chemicals waste in the private sector is frequently hindered due to technical, financial, organizational and also political reasons. Thus, the creation of an enabling environment with stimulating policies helping overcome barriers is essential for enterprises.

The supplementation of national policy instruments at regional level considering local circumstances might be advantageous. For example, a national support programme for energy-efficient manufacturing processes might be linked with cantonal subsidies for renewable energy use and information-based instruments. In general, the following instruments facilitating the implementation of innovative process optimization measures in industry can be differentiated. A mix of these instruments has proved to be beneficial:

Market-based instruments: They internalize the environmental cost, i.e. the polluter pays, and take into account the “hidden” cost of production and consumption. For instance, a VOC tax compensates for the environmental cost of ozone formation. Market-based instruments also lead to technology innovation such as VOC-free products (paints, varnishes etc.) or waste gas burners.

Regulatory instruments: Command and control instruments typically form the basis of environmental policy frameworks and should be flexible. In Switzerland for instance, the handling of synthetic refrigerants (HFC) is restricted to trained personnel and the re-use of greenhouse gas (GHG) refrigerants is promoted. However, the substitution of HFC with environmentally sound and harmless natural refrigerants based on modern technologies is not facilitated at all, showing the one-sided approach of this instrument.

Voluntary agreements: They encourage businesses to improve their resource and energy efficiency beyond regulatory measures. The use of voluntary agreements in parallel with regulations, for instance CO_2 legislation, is most useful. In some countries, an agreement between businesses and the government for the reduction of GHG emissions through energy efficiency is possible. This might lead to a more proactive behaviour and a shift from end-of-pipe thinking to increased efficiency.

Monitoring: Compliance monitoring with relevant indicators is crucial to detect violations and provide evidence to support enforcement actions. Second monitoring allows for assessing whether policies have been effective over the long term. In some European countries, regular monitoring inspections by parties contracted by the government are conducted for wastewater pollution and GHG emissions in industries.

Education: Training and outreach are relevant for the replication of resource efficiency in industry. For instance, through UNIDO’s Resource-Efficient and Cleaner Production (RECP) Programme[27], hundreds of workers were trained on the basics of industrial process optimization, and subsequent train-the-trainers programmes on RECP created the basis for further outreach in the countries involved.

Overlapping instruments: Some types of instruments overlap and can hamper each other. The enforcement of a CO_2 regulation, for instance, can lead to a switch from fossil fuel to electricity consumption for heating. Electricity, however, is to be reduced as well and regulated too (for example through a national energy law). A coordinated approach is needed to ensure policy coherence.

In the following sections, supporting policies and instruments are summarized for the countries involved in the UNIDO initiative *Innovative Approaches for the Sound Management of Chemicals and Chemical Waste*.

---

[27] UNIDO’s Resource-Efficient and Cleaner Production (RECP) Programme: http://www.unido.org/cp. html

5.1 Market-based instruments to promote efficient technologies and preventive environmental practices

Market-based instruments aim at addressing the market failure linked to environmental externalities by changing the economic conditions. Incentives or disincentives are created to encourage or discourage specific behaviours. For instance, prompting businesses to internalize costs induced by their polluting activities (for example taxation, non-compliance fines, etc.) or creating property rights (for example tradable pollution permits) are two economic instruments. Other market-based instruments can be used to stimulate the use of efficient technologies and preventive environmental practices, including [69]:

- Grants, subsidies and financial assistance (for example the National Environmental Fund in Colombia, Subsidy for Technological Conversion to avoid the use of CFCs in Chile)
- Marketable permits
- Deposits and product charges
- Harmful subsidy removal
- Reduction in taxes, duties and fees
- Targeted technical assistance
- Liability rules (Enterprises are held responsible for the environmental damage they cause which often leads them to minimizing their risks and take preventive measures.)

Because market-based instruments act as cost-effective pollution control measures, they have shown to be more economically efficient in reaching pollution reduction goals than just regulatory instruments. They allow a greater flexibility in the choice of technology and prevention strategy and may also provide the government with a source of revenue. The latter can, for instance, be used to support other environmental initiatives enhancing the sustainable development of the country. Before introducing economic instruments, the government should carefully analyze the impact of each instrument on the society and the economy. Indeed, subsidies can be used to make local industries more competitive, which may lead to reduced energy prices and therefore increases in energy consumption, shortages and pollution.

El Salvador - Market-based instruments

El Salvador has set a market incentive, known as the **“Green Seal”**, to foster the sustainable and efficient use of natural resources and to promote processes and activities preventing the contamination of the environment. The seal was conceived as an instrument of differentiation for the goods and services produced in an eco-efficient way, as well as for those exported to international markets.

El Salvador also has a **tax incentive law** for the promotion of renewable energies in electricity generation. This law promotes the realization of investment projects based on the use of renewable energy through the use of hydraulic, geothermal, wind and solar resources, as well as the biomass for power generation.

The benefits and tax incentives of this law on electricity generation projects are:

- Projects up to 10 MW: exemption from income tax for a period of 10 years
- Projects between 10 and 20 (MW): exemption from income tax for a period of 5 years
- Projects up to 20 MW: exemption from the payment of customs duties on the import of machinery, equipment, materials and supplies for the first 10 years
- Total exemption from payment of all tax revenues directly from the sale of “Certified Emission Reductions” (CERs) under the Clean Development Mechanism (CDM) or similar carbon markets

Colombian water quality policy and impacts on water quality

The Colombian water quality regulation is composed of five key elements [1]:

- **Registration and permitting**: Any discharger of liquid waste is required to obtain a discharge permit from the appropriate authority.
- **Discharge standards:** Discharge standards regulate the discharges of liquid waste in terms of location and quantity. None of these standards are industry-specific and firms may be inspected at any time to sample effluents and inspect equipment.
- **Licensing:** Prior to construction, facilities that intend to discharge liquid effluents are required to conduct an environmental impact assessment and hold a public hearing in order to obtain a licence from the environmental authorities.
- **Discharge fees:** Between 1997 and 2002, all water users discharging liquid effluents in lakes and rivers had to pay a monthly fee per unit of biochemical oxygen demand (BOD) and total suspended solids (TSS) discharged. Annual targets were set for the total quantity of BOD and TSS discharged into the same water basin by all the sources. If these targets were not met, the fees paid by the individual facilities were increased, every six months, by a factor of 0.5.
- **Quality standards:** They specify in considerable detail the maximum permissible levels of pollutants for each type of use.

Colombia’s water quality regulation strategy, and especially the discharge fee programme, showed a significant and positive impact on the water quality, as pollution loads dropped dramatically. Indeed, according to a quality evaluation realized in 2002, the implementation of discharge fees reduced the total BOD discharge by 27 per cent and total TSS discharges by 45 per cent between 1997 and 2002.

5.2 Optimization of the use of natural resources and raw materials, minimization of emissions

The optimization of the use of natural resources and raw materials protects the environment, but provides also sustainable economic and business practices. One way of optimizing the use of resources is, for instance, by minimizing waste production. By setting objectives, defining and implementing resource optimization and waste reduction strategies, companies are able to:

- Gain efficiency in production practices by achieving greater output of product per unit input of natural resources and raw materials
- Improve the financial performance of the firm by using more efficient processes to reduce the raw material and natural resource input and, as a result, the related costs
- Enhance the firm’s public image, as the environmental impact of a company and its willingness to protect the environment are important factors in its overall reputation
- Improve the quality of products manufactured by introducing new innovation and technological practices
- Meet targets set by environmental regulations, policies and standards. An environmentally responsible firm reduces its harmful emissions and impacts.

In general, governments and international organizations (for example ISO, the International Organization for Standardization) provide regulatory frameworks and guidelines to drive companies towards a more sustainable development. Below, examples of how different countries promote a more sustainable development country-wide are presented.

Egypt

The Government of Egypt has set a strategy to implement a number of policies by 2022 to diversify energy resources and rationalize the energy needs of different activities without hindering the development plans. On 10 April 2007, the Supreme Energy Council in Egypt adopted a resolution on an ambitious plan aiming at increasing the contribution of renewable energy to reach 20 per cent of the total energy generated in 2020 (8 per cent hydro power and 12 per cent wind power). This target will be achieved by private-sector participation in financing, building, owning and operating wind farms in Egypt. By 2020, a total installed wind energy capacity of 7,200 MW producing about 31 billion kWh yearly should be reached. The latter should result in annual fuel savings of about 7 million tons of oil equivalent and 17 million tons of CO_2 emissions.

Colombia

Rates of water use, as well as rates for the use of other natural resources, are indirect signals to producers to promote the rational use of these resources. Pollution fees are also a strong signal to firms that an improvement in the firm's pollutant release should be considered. Other voluntary mechanisms contribute to reaching these goals, especially in Colombian firms:

- Environmental management systems in firms
- Clean production programmes
- Eco-labels
- Sustainable procurement
- Efficiency programmes for the use and conservation of water
- Clean energy programmes
- Post-consumer and chemicals management (SAICM/OECD programmes)

Morocco

To reduce the emissions of greenhouse gases, the Moroccan energy programme will invest an estimated $18.95 billion by 2020 and will create about 50,000 jobs. It predicts that, by 2020, electrical power produced by renewable energy (solar, wind and hydro power) will account for 42 per cent of the total power produced. The main objectives of this strategy are to:

- Decrease energy dependence
- Preserve the environment
- Limit greenhouse gas emissions
- Combat climate change

5.3 Reward for good environmental performance and practices

Rewards for good environmental performance and practices are an innovative way to raise awareness of cleaner production at company, industry and national levels.

El Salvador award programmes

El Salvador has set up the National Environmental Award which is one of the incentives of the state to promote environmental management. For this award, the ministry has defined several categories. The Award for Business Efforts was established for private-sector companies which have carried out environmental restructuring in their processes. The winners receive a medal and/or an honourable mention. According to information provided by the ministry, during the period 1999-2007, 163 awards and honourable mentions were given for each of the existing categories. For the category "Business Efforts", 12 awards were granted for the same period.

The Cleaner Production Award is a strategy that the El Salvador Ministry of Environment and Natural Resources (MARN), the National Cleaner Production Centre (NCPC) El Salvador and the Central American Commission on Environment and Development (CCAD) have been promoting to the private sector to encourage and reward the companies implementing cleaner production as a tool for improving environmental performance and increase competitiveness.

The Energy Efficiency Award is a strategy that the National Energy Council and 21 organizations, including the NCPC, have been promoting to the private sector to encourage and reward the companies implementing energy efficiency as a tool for increasing competitiveness. This award was created by the programme "El Salvador is Saving Energy".

5.4 Minimization of practices leading to the exclusive use of end-of-pipe technologies

Environmental quality has often been built on regulation and authority control with specific targets and demands imposed by authorities on industries with very little flexibility with regard to reaching these requirements [70]. Such governmental control has improved the environmental conditions but also has some drawbacks such as encouraging the use of end-of-pipe technologies. Several environmental policy instruments, such as tax write-offs or financial support for environmental measures, also tend to sometimes support end-of-pipe measures and therefore work against the environmental preventive and cleaner production approach [69].

End-of-pipe technologies are generally used to control pollution rather than to prevent the pollution from happening. This approach most often comes down to fulfilling legal prescriptions and typically includes solutions like the reduction of waste and emissions through treatment units and filters. They generally also lead to higher additional costs compared to preventive and integrated solutions.

Pollution prevention and cleaner production approaches tackle the environmental problems at all levels and fields. Prevention of waste and emissions takes place at the source, and environmental protection is an integral part of process engineering. Environmental innovations are developed within the company and make environmental protection a permanent challenge. Moreover, prevention measures often help reduce costs by optimizing the material and resource consumption.

More recently, many authorities have developed a negotiated compliance approach to build cooperation strategies between the regulators and the regulated (companies, industries, etc.) to, for instance, set and enforce standards and promote an open exchange of information [70]. For example, the authorities might define the targets, but the means of reaching these targets are left to the hands of the companies [70]. This more flexible approach enables the adoption of innovative and preventive technologies.

In Colombia, for example, environmental preventive strategies are promoted in the productive general sectors through the Colombian policy of sustainable production and consumption.

Morocco – National Programme for the Prevention of Industrial Pollution (PNPPI)

In Morocco, the PNPPI allows harmonization and planning of actions that the Administration and the private sector must achieve in order to prevent pollution. It promotes and implements prevention methods by focusing on the reduction of emissions and waste as well as on the compliance with environmental laws and regulations.

The specific objectives of the program are:

- Diagnosis of the current status and the technical, institutional and regulatory framework for the prevention and fight against various forms of industrial pollution
- Identification of priority actions to be undertaken
- Development of terms of reference for studies to be carried out

5.5 Industry-lead initiatives

The various industry sectors in the economy have very different environmental impacts. The System of Environmental and Economic Accounts (SEEA), an international standard developed within the UN system, is used to assess the environmental impact of the different industries in a country and helps in identifying the domains the environmental policies should be focused on.

In Peru, illegal gold mining has been identified as a major issue in terms of environmental impact and pollution. Indeed, illegal gold mining has led to high mercury and lead contamination in the Peruvian rainforest. The Peruvian Ministry of Environment has formalized a programme to address this environmental issue.

Peru – Chemical industry-lead initiatives

In the chemical industry, different projects and technical committees aim to improve and develop the sustainable formulation, production and use of chemical substances. The following programmes and committees are managed by the Peruvian Ministry of Environment:

SAICM (Strategic Approach to International Chemicals Management)

The objective of SAICM is to strengthen the institutional capacities, regulations and techniques for managing chemicals in Peru. One output of this project was a toolkit on chemical management. The project was implemented by the Centro de Ecoeficiencia y Responsabilidad Social (CER) and the Ministry of Health with support of UNIDO from 2009 to 2011.

“Technical Group for Chemicals” (Grupo Tecnico de Sustancias Quimicas)

In 2002, the Technical Group for Chemicals (GTSQ) was formed. It is responsible for coordinating integrated actions on chemicals and implementing the Stockholm Convention on Persistent Organic Pollutants, the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade and the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal.

5.6 Regulatory instruments: command and control for environmental protection and safety

Regulatory instruments are used to set a legal framework in order to control the environmental impacts of industries by defining prohibited or permitted conduct and to establish procedures for certain environmentally risky activities. Public authorities usually set environmental standards and goals, and then inspect, monitor and punish transgressions with legal sanctions. A sound legal framework promoting environmental protection and safety is generally achieved in the following cases [1]:

- The public and private sector cooperate in the elaboration of environmental policies and regulations.
- The regulatory framework promotes continuous innovation by not specifying any particular technology.
- The decisions on innovations generated to comply with the regulation are taken by industry and not the regulatory entity.
- Environmental regulations do not promote end-of-pipe solutions but innovations designed to reduce resource consumption
- Low levels of compliance with the standards are not accepted.
- Incentives are created for the private sector, etc.

Examples of regulatory instruments for environmental protection and safety include [69]:

- Environmental standards and regulations
- Product bans and trade restrictions (for example cadmium, pesticides, CFCs)
- Quotas for raw material depletion (for example a forestry law in Costa Rica prohibiting exports of unprocessed timber)
- Facility operation standards and permits
- Liability assignment

El Salvador – Environmental regulatory instruments

El Salvador has a Cleaner Production Policy whose main objective is to incorporate ecological efficiency and effectiveness in the environmental performance and competitiveness of companies, minimizing pollution by the implementation of preventive actions in services, technologies and production processes.

During the governmental programme “País Seguro” (2004-2009), an environmental strategy was established that consisted in the establishment of voluntary agreements for cleaner production between companies and the Ministry of Environment and Natural Resources (MARN) to gradually restructure production processes into cleaner processes.

Voluntary Agreements for Cleaner Production (AVPL) are instruments of the environmental policy, based on an agreement between the private sector and the competent public administration. They are legally binding and seek to achieve specific environmental objectives and competitiveness.

Egypt –Environmental policy framework

The environmental policy of the Government of Egypt seeks to achieve environmental protection through the establishment of proper institutional, economic, legislative and technical frameworks at the local, regional, national and international levels. This is expressed through the seven directives of the policy statement of the Minister of State for Environmental Affairs (MSEA):

1. Strengthening partnerships at the national level
2. Supporting bilateral and international partnerships in the environmental fields
3. Enforcing Law 4 of 1994 and Law 9 of 2009 for the protection of the environment, and Law 102 of 1983 for natural protectorates as well as all other environmental legislation
4. Supporting institutional strengthening and capacity building for the Egyptian Environmental Affairs Agency (EEAA) and Environmental Management Units (EMUs) of the governorates
5. Supporting integrated environmental management systems
6. Integrating the use of market-based instruments in the field of environmental protection
7. Transferring and adapting environmentally friendly technologies

Within the national environmental policy framework, an Egyptian Environmental Policy Programme was initiated in 1999 with the support of the United States Agency for International Development. Based on this programme, the Government of Egypt implemented its priority environmental policy objectives and measures, through institutional and regulatory reforms, with a focus on a number of areas. These included economic and institutional constraints, cleaner and more efficient energy use, reduced air pollution, improved solid waste management, sustainable tourism as well as nature conservation.

Within this policy framework, institutional and regulatory reforms are carried out, aiming at the implementation of national environmental policy objectives and measures. The implementation of the environmental policies of the Government of Egypt, as expressed by the policy framework and directives of the MSEA, is undertaken with regard to four main principles underlying environmental management and protection initiatives:

1. Strengthening the integrative capacity of central and local government
2. Strengthening of public-private partnerships
3. Partnerships with environmental non-governmental organization
4. Integration of gender issues in environmental policies and programmes

6 Funding of innovations

In many countries, the lack of attractive financial conditions is a barrier to comprehensive investments in new technologies in companies, thus also limiting the success of clean, innovative and environmentally sound technologies. That is why numerous alternative finance instruments were developed in the past to facilitate industrial investments. In the following section, selected instruments are presented as examples in countries within the scope of the present UNIDO project.

6.1 Funding in Peru

6.1.1 Green Credit Trust Fund

The Green Credit Trust Fund (GCTF) was initiated in Peru in 2004 by the State Secretariat for Economic Affairs (SECO). It is oriented towards supporting sustainable industrial production initiatives in small and medium enterprises. The GCTF supports projects related to eco-efficiency and technological reconversion up to a maximum amount of $1 million worth of credit. To benefit from the fund, the enterprise must seek to improve its processes through green technologies. Projects that only aim to fulfil legal requirements are not supported by the credit fund.

To qualify for the GCTF, the enterprise must be registered in Peru, have a maximum of 25 per cent of foreign capital and be legally independent from any international organization. The GCTF is available to manufacturing companies but SMEs in this sector must not own more than $8.5 million worth of fixed assets and must not have more than 500 employees.

The company first applies for the credit through one of three different intermediary financing institutions (Banco de Crédito del Perú, Interbank and Scotiabank del Perú). Then, the enterprise selects environmental indicators, in consultation with the Peruvian NCPC. Next, an evaluation of whether the new technology will improve the production and reduce the environmental impact of the company is undertaken. Once the new technology is installed, the indicators are monitored and a report based on the improvements is sent to SECO.

SECO can also provide a guarantee of 50 per cent if required. If the report shows significant improvements of the enterprise’s environmental performance, the company receives a reimbursement from SECO.

The reimbursement levels are based on the credit amount or the investment amount, whichever the smaller of the two. The levels are the following:

- 15 per cent reimbursement for 30 per cent worth of environmental improvement
- 25 per cent reimbursement for 50 per cent worth of environmental improvement

There are no intermediate levels for the reimbursement.

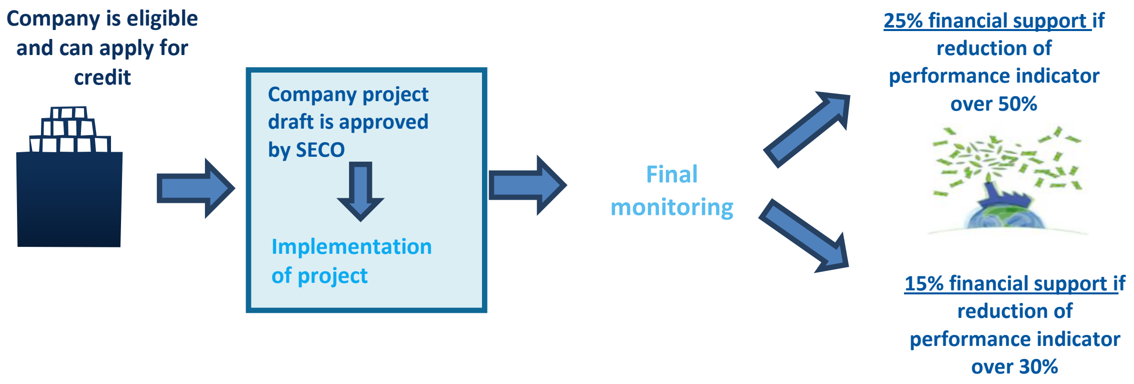


Figure 6-1 : The Green Credit Trust Fund [74]

Since the beginning of the initiative, 17 projects have been approved, with a total amount of more than $4.3 million.

The GCTF concept has proven to be operational. The success is embedded in combining a financial instrument with Sustainable Enterprise Development (SED) centres which have extensive environmental know-how (for example in Peru Centro de Ecoeficiencia y Responsabilidad Social (CER)). With the GCTF, no direct interferences in finance markets occur, which allows banks to assume their role as agents to analyze the creditworthiness of investments.

Most of the investments prove to be win-win solutions improving the economic aspects as well as reducing the environmental impacts of the companies. Some projects even improve social aspects, thus clearly demonstrating the potential of environmentally sound technologies (ESTs). With the GCTF, SED centres get access to clients who potentially have projects related to cleaner production.

6.2 Funding in El Salvador

6.2.1 FONDEPRO

The Productive Development Fund (Fondo de Desarallo Productivo, FONDEPRO) is an incentive created to promote the development of quality, productivity and innovation, and to support the adoption and implementation of technological improvements leading to cleaner production processes. The fund supports the competitive strengthening of small and medium enterprises by co-financing up to 60 per cent of the total cost of a project or timely initiative.

The fund has two co-financing models:

- Fast track model: support of up to $15,000 for a project focused on a specific activity
- Support of up to $100,000 for a project combining multiple activities

Annual sales must not exceed $7 million and the enterprise must be located in El Salvador.

From 2002 to 2008, 718 projects were supported through the fast track model, which represents a placement of more than $1.3 million.

6.2.2 BANDESAL-KfW Environmental Conversion Line

El Salvador’s bank for development BANDESAL (Banco de Desarollo de El Salvador) contracted with the German development bank KfW a three-phase credit line for the environmental conversion of companies. For the first phase from 2007 to 2010, $10 million were released, with $500,000 non-refundable and allocated for technical assistance in environmental projects. For the second phase from 2011 to 2013 and the third phase, respectively $27 million and $50 million were released.

The main objectives of the programme are to contribute to the reduction of environmental pollution, to promote the efficient use of natural resources by small and medium enterprises and to deepen the financial system by establishing long-term instruments for environmental investments for companies located in El Salvador. This programme supports entrepreneurs willing to invest in more efficient and environmentally friendly production processes. For an environmental project, the credit limit is set to $500,000. For a project concerning renewable energies, a credit of a maximum of $4 million can be provided (projects of more than $500,000 require an authorization by KfW). The credit finances up to 80 per cent of the value of the investment and has a fixed yearly interest rate of 3.6 per cent for the life of the loan.

With the technical support of the NCPC, the credit line has assisted 28 small and medium enterprises since 2010.

The benefits obtained in these 28 companies are, in average, the following:

- Energy consumption reduced by 6.7 per cent
- Fuel oil consumption reduced by 8.4 per cent
- Savings of $1.1 million achieved per year
- Investments of $1.3 million
- 2,300 tons of CO_2 emissions avoided per year

6.3 Funding in Egypt

6.3.1 Private Public Sector Industry Project

The Private Public Sector Industry (PPSI) Project aims to protect the environment by contributing to the reduction of industrial pollution. PPSI focused on private and public industrial establishments in Upper Egypt and the Delta, and operated from 2008 to 2012. PPSI was implemented by the Egyptian Environmental Affairs Agency and supported by KfW under the German financial cooperation with Egypt.

Grants covering 20 to 30 per cent of the pollution abatement investment costs, with a maximum of $1 million, were provided for eligible sub-projects. Preferential treatment was applied to SMEs (companies with a turnover of less than $2.8 million) and at least 30 per cent of the investment funds were allocated for SMEs. The second phase of PPSI ended in 2012. The third phase has not yet started.

6.3.2 Environmental Compliance Office Revolving Fund Programme

The Environmental Compliance Office (ECO) was set up in 2002 by the Egyptian Government and the Danish International Development Agency (DANIDA) to assist in achieving compliance in industry. A cooperation agreement was signed in February 2005 between the Egyptian Environmental Affairs Agency (EEAA), the Federation of Egyptian Industries (FEI) and the National Bank of Egypt (NBE) for the purpose of operating the ECO Revolving Fund to invest in new equipment.

DANIDA provided funds equivalent to more than $11 million to be allocated within the industrial sector to support initiatives aiming at abating pollution, encouraging safe working conditions and ensuring environmental legislative compliance. The revolving fund provided enterprises with the opportunity to make economic benefits and ensure proper compliance with environmental laws.

Small and medium enterprises being members of the FEI are eligible to apply. Loans can reach up to $420,000 per enterprise with a 2.5 per cent interest rate per year. Loans are repaid over 5 years and funds are reused for financing new cleaner production initiatives in other enterprises.

6.4 Funding in Morocco

6.4.1 National Fund for the Environment (FNE)

The National Fund for the Environment is a financial incentive instrument established in 2004 for the protection and valorization of the environment. This fund aims at:

- Funding programmes for domestic and industrial water treatment
- Financing solid waste management programmes
- Financing pilot projects for the environment

6.4.2 Fund for Industrial Depollution (FODEP)

FODEP promotes the environmental upgrading through technical and financial support of industrial companies. The subsidy covers up to 40 per cent of the investment, with a maximum of $625,000.

6.4.3 Voluntary Mechanism of Industrial Wastewater Treatment

This programme is funded by the Moroccan state and aims at encouraging industrial companies to invest in wastewater treatment processes. Industrial volunteers can benefit from a subsidy covering up to 40 per cent of the investment cost, with a maximum amount of $625,000 for individual projects and $1.25 million for collective projects.

6.4.4 Business Advisory Service Programme

Launched by the European Bank for Reconstruction and Development (EBRD), this programme aims at developing the expertise and local consultancy through technical and financial support to consulting assignments. The financial support covers 50 to 75 per cent of the mission’s expenses. Moroccan companies with a turnover of less than $68.2 million can benefit from this programme. Beneficiaries can be supported for the realization of:

- Technical studies: planning/architectural design, space optimization, IT infrastructure design, selection of machinery and equipment, installation, training
- Quality management system and certification: ISO 9000, Hazard Analysis and Critical Control Points (HACCP)
- Energy efficiency and environmental impact reduction: energy audit, mechanism for clean growth, renewable energy, environmental impact assessment, ISO 14000 implementation

7 Where do I find support?

The identification and implementation of innovative solutions and alternatives for chemicals and chemical waste management require extensive know-how of logistic processes, technical requirements, optimization techniques, standards and legal requirements. If a thorough analysis of possible innovations cannot be completely undertaken by a competent and experienced team within the company, the participation of external experts is highly recommended.

For assistance on innovative chemical solutions, the National Cleaner Production Centre (NCPC) Programme offers services such as RECP assessments on energy and resource efficiency, technology gap assessments and generation of process optimization measures.

NCPC representatives in the five countries involved in the project *Innovative Approaches for the Sound Management of Chemicals and Chemical Waste* can be reached at:

COLOMBIA

Mr. Carlos Fernando Cadavid Restrepo - Director of Projects
carlos.cadavid@cnpml.org

Mr. Carlos Arango - Executive Director
carlos.arango@cnpml.org

Carrera 46 No 56 -11Piso 8 Edificio Tecnoparque Medellín
Colombia

Tel.: (57 4) 251 7343
Fax: (57 4) 513 09 30
www.cnpml.org
correo@cnpml.org
www.produccionmaslimpia-la.net

EGYPT

Mr. Ali Abo Sena - Director
abosena@encpc.org

Egypt National Cleaner Production Center
26 A Sherif St. - Emobilia Building - Down Town, Cairo,
Egypt

Phone: (202) 23916154
www.encpc.org

El Salvador

Ms. Yolanda Salazar De Tobar - Director
ysalazar@cnpml.org.sv

Fundación Centro Nacional de Producción mas Limpia
Calle El Lirio #19, Colonia Maquilishuat, San Salvador, El Salvador

Tel.: (503) 2264-3210 (503) 2264-4622
Fax: (503) 2264-3210, (503) 2263-9448
cnpml@cnpml.org.sv
www.cnpml.org.sv
www.produccionmaslimpia-la.net

MOROCCO

Mr. Manwah Ayassor – PM
manwah.ayassor@cmpp. co.ma

Moroccan Cleaner Production Centre (CMPP)
23, Bd Med Abdouh, quartier Palmiers,
20100, Casablanca, Morocco

Tel: (+212) 5 22 99 70 53
Fax: (+212) 5 22 98 15 31
www.cmpp. ma

PERU

Mr. Marcos Alegre - Director
malegre@grupogea.org.pe

Centro de Ecoeficiencia y Responsabilidad Social (CER)

Av. Chorrillos 150 - Chorrillos
Lima, Perú

Phone: (511) 467 1958 467 1802
Fax: (511) 467 1975
contacto@cer.org.pe
www.cer.org.pe
www.produccionmaslimpia-la.net

Further information and contacts please refer to the UNIDO NCPC website at www.unido.org.

8 Bibliography

1. UNIDO, UNIDO Green Industry – Policies for supporting green industry (2011)
2. Strategic Approach to International Chemicals Management (SAICM), Introducing SAICM (2014)
3. European Commission: Reference Document on Best Available Techniques in the Production of Polymers, 2007
4. Sulzer Chemtech ltd.: Polymer Production Technology
5. European Commission Integrated Pollution Prevention and Control (IPPC): Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry, 2003
6. European Commission Integrated Pollution Prevention and Control (IPPC): Reference Document on the General Principles of Monitoring, 2003
7. European Commission Integrated Pollution Prevention and Control (IPPC): Reference Document on Best Available Techniques in Common Waste Water and Waste Gas Treatment / Management Systems in the Chemical Sector, 2003
8. Bauer S., Dr. Joas R., Dr. Hofbauer P., Tebert C., Krause S., Jepesen D.: Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC), European Commission – DG Environment, 2009
9. Nester J.: Technology Selection Criteria for VOC Control, Nestec, Inc., 2006
10. Moretti E.: Reduce VOC and HAP Emissions, Baker Environmental, Inc., 2002
11. Adhesives&Glues: http://www.adhesiveandglue.com/modified-silane.html
12. Asahi Kasei (Japan): http://www.asahi-kasei.co.jp/chemicals/en/license/page01.html
13. Corbion (Netherlands): http://www.purac.com/EN/Bioplastics/PLA-applications.aspx
14. US EPA: http://www2.epa.gov/green-chemistry/2007-designing-greener-chemicals-award
15. Galactic (Belgium): http://www.loopla.org/cradle/cradle.htm
16. 3M Solutions (Germany): http://solutions.3mdeutschland.de/wps/portal/3M/de_DE/EU_AdMD/Dyneon_Fluoropolymers/
17. Akzo Nobel Polymer Chemicals: https://www.akzonobel.com/polymer/our_products/noxol_everplus_antifouling_agents/
18. INEOS Group: http://www.ineos.com/Products/?bu=INEOS%20Technologies&m=PVC%20Additives&f=1
19. Membrane Technology & Research: http://www.mtrinc.com/polyvinyl_chloride_production.html
20. Ebewele R. O. (2000). Polymer science and technology by CRC Press LLC v p.544
21. PROBES, (2008). Development of national emission standards for petrochemical plants, Central Pollution Control Board, p.176
22. Moretti E.C. (June 2002). Reduce VOC and HAP emissions, CEP Magazine
23. Plastics Europe: Plastics – the Facts 2012
24. IHS: www.ihs.com/chemical
25. Uhde Inventa Fischer (2014): http://www.uhde-inventa-fischer.com/service-navigation/media/news/
26. Vinyl Loop: http://www.vinyloop.com/en/
27. United Kingdom (UK) Chemicals Stakeholder Forum with a group of authors: Guide to chemical services – an information note from the UK Chemicals Stakeholder Forum
28. UNIDO Sector Study: Potentials for Chemical leasing in selected cleaning operations, prepared by BiPRO GmbH, Germany

29. Jakl T., Schwager P.: Chemical Leasing Goes Global, Federal Ministry of Agriculture, Forestry, Environment and Water Management of Austria and United Nations Industrial Development Organisation (UNIDO) (2008)
30. ACCENTURE, Sharpening business models helps chemical companies achieve high performance (2009)
31. European Commission, Directive 96/82/EC (Seveso II)
32. UNEP, Flexible Framework for Addressing Chemical Accident Prevention and Preparedness (2010)
33. UNEP, Responsible Production Booklet – A Framework for Chemical Hazard Management for Small and Medium Sized Enterprises (2009)
34. European Commission (EC), Major Accidents Hazards Bureau (MAHB), Guidelines on a Major Accident Prevention Policy and Safety Management System
35. Cheremisinoff N.F.: Practical guide to industrial safety: Methods for Process Safety Professionals, Marcel Dekker Inc. New York / Basel (2001)
36. Gabbar H.A. & Suzuki K.: The Design of a Practical Enterprise Safety Management System, Kluwer Academic publishers, Dordrecht / Boston / London (2004).
37. AIChE, Special Process Hazards, in Dow's Fire & Explosion Index Hazard Classification Guide, Seventh Edition, John Wiley & Sons, Inc., Hoboken, NJ, USA.(1994)
38. TNO Purple Book (1999): www.tno.nl
39. ISSA, Maintenance and Changes in Plants with High Safety Requirements: Practical Guidance (2007)
40. EPA, General Risk Management Program Guidance, Chapter 7 (2004), Retrieved from http://www.epa.gov/oem/content/rmp/rmp_guidance.htm
41. UNEP, Flexible Framework for Addressing Chemical Accident Prevention and Preparedness (2010)
42. UNECE **(**United Nations Economic Commission for Europe), GHS, (2013)
43. UNEP, Responsible Production Guidance and Toolkit (2009)
44. GTZ Chemical Management Guide for Small and Medium Sized Enterprises (2007)
45. HAS (Health and Safety Authority), Ireland, Your steps to chemical safety, A guide for small business (undated)
46. DUKE University, Occupational and Environmental Safety Office, Safe use of chemicals
47. Sicherheitsinstitut (Switzerland): Lagerung gefährlicher Stoffe, Leitfaden für die Praxis, überarbeitete Auflage (2011), Retrieved from http://www.kvu.ch/fr/themes/stockage-de-liquides
48. Vereinigung Kantonaler Feuerversicherung (Switzerland): Directive de protection incendie, liquides inflammables (2003), Retrieved from http://www.vkf.ch
49. United Nations: Globally Harmonized System of Classification and Labelling of Chemicals (GHS), 2003, last revision 2013
50. United Nations, UN Recommendations on the Transport of Dangerous Goods, last revision 2013
51. United Nations, European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR), 1957, last revision 2013
52. EU, ATEX norms based on european directives 94/9CE, 1994 and 1999/92/CE, 1999
53. ECA Incendie et éléments naturels: Distances de sécurité. Cours spécialiste en protection incendie AEAI (2011)
54. L'usine nouvelle, Bacs de rétention en plastique, Retrieved from http://www.usinenouvelle.com/expo/bacs-de-retention-en-p-o1203.html (2013)
55. Neosys, Formation matières dangereuses (2011)
56. CFPA Europe, Fire protection on chemical manufacturing sites. European Guideline No 18 (2013)
57. CFPA Europe, Safety distances between waste containers and buildings. European Guideline No 7 (2011)
58. CFPA Europe, Introduction to qualitative fire risk assessment. European Guideline No 4 (2003).
59. Institut de Sécurité, Concepts de protection incendie. Fiche 1101-00.f. (1996)
60. Protection displays, Emergency evacuation plan, Retrieved from http://www.evacmaps.com/ (2002).
61. DEFRA UK, Guidance on applying the waste hierarchy (2011)
62. GIZ, Manual on industrial Hazardous Waste Management (2012)

63. Hazardous Waste Management Inspection Manual, Egypt, Ministry of State for Environmental Affairs and Egyptian Environmental Affairs Agency (2002)
64. Environment Agency of the UK, A guide to the hazardous waste regulations for small businesses
65. IFC, General HSE Guidelines (2007)
66. Campus Environmental Resource Centre, University of Cincinnati, Retrieved from http://www.campuserc.org/virtualtour/waste/best/Pages/default.aspx
67. UNEP, Guidelines on BAT and Guidance on BEP, section VI, Annex C part III source category, fossil fuel-fired utilities and industrial boilers (2007)
68. Schult S., M. J.: Energie einfach besser nutzen, Carl Schünemann Verlag, Bremen (2013)
69. UNIDO NCPC Program, Development of CP Policies: Approaches and Instruments (2002)
70. Lennart N., et al.: Cleaner Production – Technologies and tools for resource efficient production (2007)
71. Weslynne A., et al.: Best practices in cleaner production promotion and in implementation for smaller enterprises (2002)

72. VKF/AEAI: Directive protection incendie, liquides inflammables, Switzerland, (2003)
73. IPTS: Chemical Product Services in the European Union, SAFECHEM
74. CSD Engineers, Switzerland (2015)
75. UNIDO, Environment branch, Vienna (2015)
76. Suva: Bouteilles à gaz – Entrepôts, rampes, systèmes de distribution de gaz, Switzerland (2007)
77. DEFRA,Guidance on applying the waste hierarchy, UK (2011)
78. University of Cincinnati: Campus Environmental Resource Centre, USA (2014)
79. IFC: General HSE Guidelines (2007)
80. Blackman W.C.: Basic Hazardous Waste management (3rd edition), CRC Press LLC, USA (2001)
81. Cheremisinoff N.F.: Practical guide to industrial safety: Methods for Process Safety Professionals, USA/Switzerland (2001)
82. Sicherheitsinstitut: Lagerung gefährlicher Stoffe, Leitfaden für die Praxis, Überarbeitete Auflage 2011, Switzerland, (2011)

Appendices

Appendix 1: Chemical resistance selection chart for protective gloves

The ratings are abbreviated as follows: VG: Very Good; G: Good; F: Fair; P: Poor (not recommended). Chemicals marked with an asterisk (*) are for limited service.

Table A2-1: Chemical resistance selection chart [based on 81]

Chemical	Neoprene	Latex/Rubber	Butyl	Nitrile
Acetaldehyde*	VG	G	VG	G
Acetic acid	VG	VG	VG	VG
Acetone*	G	VG	VG	P
Ammonium hydroxide	VG	VG	VG	VG
Amy acetate*	F	P	F	P
Aniline	G	F	F	P
Benzaldehyde*	F	F	G	G
Benzene*	P	P	P	F
Butyl acetate	G	F	F	P
Butyl alcohol	VG	VG	VG	VG
Carbon disulphide	F	F	F	F
Carbon tetrachloride*	F	P	P	G
Castor oil	F	P	F	VG
Chlorobenzene*	F	P	F	P
Chloroform*	G	P	P	F
Chloronaphthalene	F	P	F	F
Chromic acid (50%)	F	P	F	F
Citric acid (10%)	VG	VG	VG	VG
Cyclohexanol	G	F	G	VG
Dibutyl phthalate*	G	P	G	G
Diesel fuel	G	P	P	VG
Diisobutyl ketone	P	F	G	P
Dimethylformamide	F	F	G	G
Dioctyl phthalate	G	P	F	VG
Dioxane	VG	G	G	G
Epoxy resins, dry	VG	VG	VG	VG
Ethyl acetate*	G	F	G	F
Ethyl alcohol	VG	VG	VG	VG
Ethyl ether*	VG	G	VG	G

Chemical	Neoprene	Latex/Rubber	Butyl	Nitrile
Ethylene dichloride*	F	P	F	P
Ethylene glycol	VG	VG	VG	VG
Formaldehyde	VG	VG	VG	VG
Formic acid	VG	VG	VG	VG
Freon 11	G	P	F	G
Freon 12	G	P	F	G
Freon 21	G	P	F	G
Freon 22	G	P	F	G
Furfural*	G	G	G	G
Gasoline, leaded	G	P	F	VG
Gasoline, unleaded	G	P	F	VG
Glycerin	VG	VG	VG	VG
Hexane	F	P	P	G
Hydrazine (65%)	F	G	G	G
Hydrochloric acid	VG	G	G	G
Hydrofuoric acid (48%)	VG	G	G	G
Hydrogen peroxide (30%)	G	G	G	G
Hydroquinone	G	G	G	F
Isooctane	F	P	P	VG
Kerosene	VG	F	F	VG
Ketones	G	VG	VG	P
Lacquer thinners	G	F	F	P
Lactic acid (85%)	VG	VG	VG	VG
Lauric acid (36%)	VG	F	VG	VG
Lineolic acid	VG	P	F	G
Linseed oil	VG	P	F	VG
Maleic acid	VG	VG	VG	VG
Methyl alcohol	VG	VG	VG	VG
Mehylamine	F	F	G	G
Methyl bromide	G	F	G	F
Methyl chloride*	P	P	P	P
Methyl ethyl ketone*	G	G	VG	P
Methyl isobutyl ketone*	F	F	VG	P
Methyl metharcrylate	G	G	VG	F
Monoethanolamine	VG	G	VG	VG
Morpholine	VG	VG	VG	G

Chemical	Neoprene	Latex/Rubber	Butyl	Nitrile
Naphtalene	G	F	F	G
Napthas, aliphatic	VG	F	F	VG
Napthas, aromatic	G	P	P	G
Nitric acid*	G	F	F	F
Nitric acid, red and white fuming	P	P	P	P
Nitromethane (95.5%)*	F	P	F	F
Nitroprophane (95.5%)	F	P	F	F
Octyl alcohol	VG	VG	VG	VG
Oleic acid	VG	F	G	VG
Oxalic acid	VG	VG	VG	VG
Palmitic acid	VG	VG	VG	VG
Perchloric acid (60%)	VG	F	G	G
Perchloroethylene	F	P	P	G
Petroleum distillates (naphtha)	G	P	P	VG
Phenol	VG	F	G	F
Phosphoric acid	VG	G	VG	VG
Potassium hydroxide	VG	VG	VG	VG
Propyl acetate	G	F	G	F
Propyl alcohol	VG	VG	VG	VG
Propyl alcohol (iso)	VG	VG	VG	VG
Sodium hydroxide	VG	VG	VG	VG
Styrene	P	P	P	F
Styrene (100%)	P	P	P	F
Sulphuric acid	G	G	G	G
Tannic acid (65)	VG	VG	VG	VG
Tetrahydrofuran	P	F	F	F
Toluene*	F	P	P	F
Toluene diisocyanate (TDI)	F	G	G	F
Trichloroethylene*	F	F	P	G
Triethanolamine (85%)	VG	G	G	VG
Tung oil	VG	P	F	VG
Turpentine	G	F	F	VG
Xylene*	P	P	P	F

Appendix 2: Storage

Storage incompatibilities

Table A3-1: Storage of hazardous substances commonly used in industry [based on 82]

		Formic acid	Solution of ammonia	Solution of iron chloride (III)	Solution of iron chloride (III) sulfate	Acetic acid	Hydrofluoric acid	Solution of potassium hydroxide	Solution of sodium hydroxide	Solution of sodium hydrogensulfite	Solution of sodium hypochlorite	Peracetic acid	Phosphoric acid	Nitric acid	Hydrochloric acid	Sulphuric acid	Hydrogen peroxide
	Storage category	**8**	**8**	**8**	**8**	**3**	**6.1**	**8**	**8**	**10/12**	**5**	**5**	**8**	**5**	**8**	**8**	**5**
Formic acid	**8**	⬜	🟨	🟩	🟩	🟩	🟩	🟨	🟨	🟥	🟥	🟨	🟩	🟥	🟩	🟥	🟥
Solution of ammonia	**8**	🟨	⬜	🟨	🟨	🟨	🟨	🟥	🟥	🟨	🟨	🟥	🟨	🟥	🟨	🟨	🟨
Solution of iron chloride (III)	**8**	🟩	🟨	⬜	🟩	🟩	🟩	🟨	🟨	🟥	🟥	🟨	🟩	🟩	🟩	🟩	🟨
Solution of iron chloride (III) sulfate	**8**	🟩	🟨	🟩	⬜	🟩	🟩	🟨	🟨	🟥	🟥	🟨	🟩	🟩	🟩	🟩	🟨
Acetic acid	**3**	🟩	🟨	🟩	🟩	⬜	🟩	🟨	🟨	🟥	🟥	🟨	🟩	🟥	🟩	🟩	🟥
Hydrofluoric acid	**6.1**	🟩	🟨	🟩	🟩	🟩	⬜	🟨	🟨	🟥	🟥	🟥	🟩	🟩	🟩	🟥	🟩
Solution of potassium hydroxide	**8**	🟨	🟥	🟨	🟨	🟨	🟨	⬜	🟩	🟨	🟩	🟥	🟨	🟨	🟨	🟨	🟨
Solution of sodium hydroxide	**8**	🟨	🟥	🟨	🟨	🟨	🟨	🟩	⬜	🟨	🟩	🟥	🟨	🟨	🟨	🟨	🟨
Solution of sodium hydrogensulfite	**10/12**	🟥	🟨	🟥	🟥	🟥	🟥	🟨	🟨	⬜	🟥	🟥	🟥	🟥	🟥	🟥	🟨
Solution of sodium hypochlorite	**5**	🟥	🟨	🟥	🟥	🟥	🟥	🟩	🟩	🟥	⬜	🟥	🟥	🟥	🟥	🟥	🟨
Peracetic acid	**5**	🟨	🟥	🟨	🟨	🟨	🟥	🟥	🟥	🟥	🟥	⬜	🟥	🟥	🟥	🟥	🟥
Phosphoric acid	**8**	🟩	🟨	🟩	🟩	🟩	🟩	🟨	🟨	🟥	🟥	🟥	⬜	🟩	🟩	🟩	🟩
Nitric acid	**5**	🟥	🟥	🟩	🟩	🟥	🟩	🟨	🟨	🟥	🟥	🟥	🟩	⬜	🟥	🟥	🟥
Hydrochloric acid	**8**	🟩	🟨	🟩	🟩	🟩	🟩	🟨	🟨	🟥	🟥	🟥	🟩	🟥	⬜	🟥	🟩
Sulphuric acid	**8**	🟥	🟨	🟩	🟩	🟩	🟥	🟨	🟨	🟥	🟥	🟥	🟩	🟥	🟥	⬜	🟩
Hydrogen peroxide	**5**	🟥	🟨	🟨	🟨	🟥	🟩	🟨	🟨	🟨	🟨	🟥	🟩	🟥	🟩	🟩	⬜

Safety distances

Table A3-2: Evaluation of the neighbouring risk [based on 72]

Type of storage building	Neighbouring building activity		
	Low danger[28]	Medium danger[29]	High danger[30]
Specifically resistant to fire	Low	Low	Low
Non-flammable (concrete)	Low	Medium	High
Flammable (wood)	Medium	High	High

Table A3-3: Safety distance in metres between outside warehouses and buildings, structures and facilities [based on 72]

Neighbouring risks (Table A3-2)	Storage in containers (in litres)					
	Categories F1 and F2			Categories F3, F4 and F5		
	Up to 5,000	Up to 50,000	Above 50,000	Up to 5,000	Up to 50,000	Above 50,000
Low	5	10	15	-	5	8
Medium	10	15	20	5	8	12
High	15	20	25	8	12	15

Table A3-4: Safety distance in metres between unburied tanks and buildings, structures and facilities [based on 72]

Neighbouring risks (Table A3-2)	Storage in tanks (in m^3)					
	Categories F1 and F2			Categories F3, F4 and F5		
	Tank resistant to overpressure	Vertical tank		Tank resistant to overpressure	Vertical tank	
		Up to 500	Above 500		Up to 500	Above 500
Low	12	20	30	6	10	15
Medium	16	25	35	8	12	18
High	20	30	40	10	15	20

---

[28] Production, treatment and storage of non-flammable materials

[29] Engineering workshops, car repair, offices, apartments

[30] Storage and treatment of hazardous materials, wood processing, printing, professional accommodation, buildings with space for a large number of occupants

Appendix 3: Fire protection

Table A4-1: Main hazardous product classes associated with fire or explosion hazards

Hazard class	GHS[31] pictogram	Hazard statement codes
Explosives		H200 – Unstable explosive H201 – Explosive; mass explosion hazard H202 – Explosive; severe projection hazard H203 – Explosive; fire, blast or projection hazard H204 – Fire or projection hazard
Flammable gases		H220 – Extremely flammable gas
Aerosols		H222 – Extremely flammable aerosol H223 – Flammable aerosol H229 – Pressurized container; may burst if heated
Oxidizing gases		H270 – May cause or intensify fire; oxidizer
Gas under pressure		H280 – Contains gas under pressure; may explode if heated
Flammable liquids		H224 – Extremely flammable liquid and vapour H225 – Highly flammable liquid and vapour H226 – Flammable liquid and vapour
Flammable solids		H228 – Flammable solid
Substances and mixtures which in contact with water emit flammable gases		H260 – In contact with water releases flammable gases which may ignite spontaneously H261 – In contact with water releases flammable gases
Oxidizing liquids or solids		H271 – May cause fire or explosion; strong oxidizer H272 – May intensify fire; oxidizer

---

[31] Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

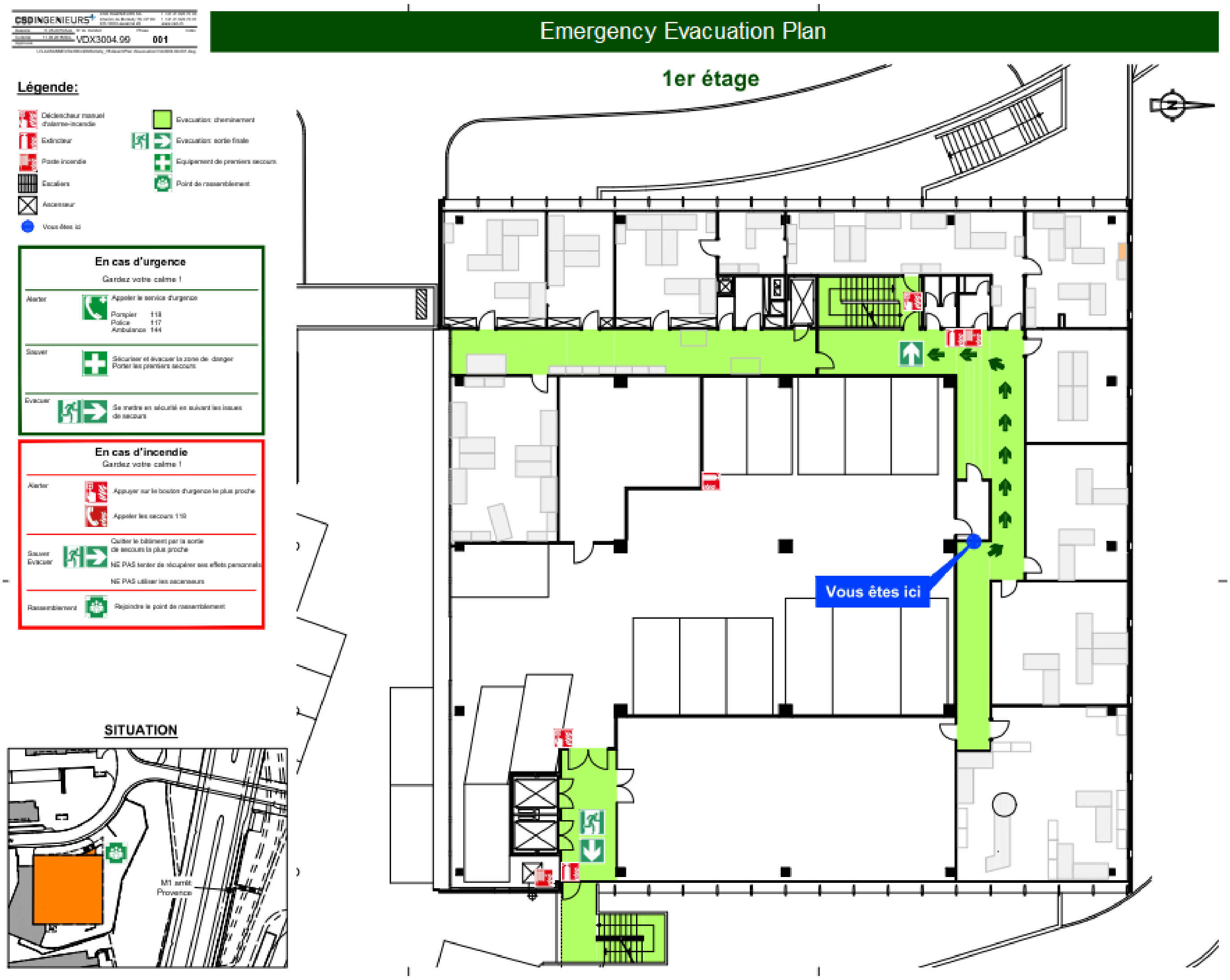


Figure A4-1: Emergency plan [74].