INNOVATIVE DIGITAL WATERMARKS AND GREEN SOLVENTS FOR THE RECOVERY AND RECYCLING OF MULTI-LAYER MATERIALS

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Safety and Health Risk Management Procedures

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2 Executive Summary

One of the key tasks in developing new recycling and recovery processes is to make an environmental and health and safety assessment. This is particularly important in the case of the Sol-Rec2 process, which combines novel chemical and physical treatment stages in a unique process that offers substantial benefits over existing approaches. Consequently, one of the main activities in Work Package 7, is a task to identify the environmental, health and safety (EHS) issues associated with each of the stages and materials used in the Sol-Rec2 process. More specifically, this analysis is related to both the individual processes and the combination of the new technologies, in order to identify and, ideally, avoid any realised risks to personnel, society and the environment.

In the work reported in this deliverable, guidelines, risk minimisation procedures and performance indicators for the integrated Sol-Rec2 processes, including the primary and secondary routes, have been investigated and elaborated. These have been developed in the context of the details provided by the project partners on the basis of relevant European Legislation and on a comparative risk assessment regarding equivalent industrial processes. Information from each of the different stages of the project has been compiled, reviewed and incorporated into the EH&S Guidelines for the safe and an environmentally friendly operation of the Sol-Rec2 pilot plant. A substantial part of the document relates to the risk assessment and minimisation approaches that should be applied when scaling up the Sol-Rec2 process to the Pilot Plant scale.

This initial version of the deliverable was completed at the end of month 14 of a 36-month project. It is thus highly likely that the process will evolve further during the remainder of the project. Consequently, this document will be reviewed and updated as appropriate before a final version is completed at the end of the project. The guidelines and risk minimisation procedures detailed herein will be made publicly available through the project website and shared with the ETPIS platform (EU Technology Platform Industrial Safety).

3 Health and Safety Considerations for Plastics Recycling

3.1 Overview

The recycling of plastics, typically involves multiple activities from their collection and sorting to the production of a usable end product and the disposal of any waste. These activities require various treatment process stages often using a range of a mechanical comminution equipment. In the case of the Sol-Rec2 process, there will be a combination of initial mechanical stages followed by novel chemical treatments, which also require the use of power, heating and washing operations. These will then be followed by further mechanical processing operations, also involving the use of chemical additives, to produce a range of recyclates with properties tailored for specific applications. There will thus be a significant potential for health and safety issues throughout the process, even though the specific ionic liquids used in the novel recyclate separation stages of the process are likely to be relatively benign. This section gives an introductory overview of the general health and safety risks associated with plastics recycling and the following sections than cover the individual process and material aspects that are specifically pertinent to the Sol-Rec2 process in more detail.

While recycling and reuse of plastics offers significant benefits, it must also be appreciated that there can often be significant health and safety aspects that must be addressed by those engaged in recycling operations. In the case of the plastics that will be recycled by the Sol-Rec2 process, it is quite possible that the waste plastic products that are collected for recycling may contain undesirable, or even hazardous biological and chemical contaminants which could compromise the future safe use of the recyclate and possibly also present problems for those operating the recycling processes. Workers may be exposed to hazardous substances when sorting and processing such waste plastics. Ultimately, if waste plastic items containing such contaminants are not identified and removed, the outcome might be the production of recyclate containing harmful materials that could lead to health and safety issues for end users as well as the recyclers. For example, one such issue could be the recycling of drugs and medicines found in part used or unused medicine blister packs. It will, therefore, be vitally important to ensure that only completely empty and clean medicine blister packs enter the recycling process. This can largely be achieved by implementing checks and controls early on in the process so that collection schemes only accept empty blister packs. However, this alone is unlikely to give complete certainty that no part-used or unused blister packs are sent for recycling and there will need to be further scrutiny as part of the initial screening and sorting processes at the recycling plant. The same, of course, is also true with contamination from food in food packaging, since any residues can negatively impact the recycling process and degrade the quality of any recovered polymers.

Another area where there are potentially important health and safety risks is with the processing and recycling of polyvinyl chloride, which is a widely used major component of medicine blister packs. There are numerous issues with the recycling of PVC, such as the possible emission of hydrogen chloride at elevated temperatures, and these aspects are covered in greater detail in a subsequent dedicated section.

Within a plastics recycling facility there are many operations that need careful consideration and attention in order to minimise the health and safety issues and thus the impact on workers. Plastic recycling processes have the potential to generate both environmental and occupational health risks. For example, there is the strong possibility that operators may be exposed to both microbes and bioaerosols during the initial waste plastic sorting and cleaning stages of the process. The use of extrusion and injection moulding equipment, which operates at relatively high temperatures, can lead to high levels of vapours and particulate emissions during operation. These can include the emission of a range of volatile and semi-volatile organic compounds (VOCs and SVOCs) from the molten polymers during any actual extrusion and injection moulding operations that may form part of the overall recycling operation. The actual type and level of these particulate and gaseous emissions will be heavily dependent on the quality and cleanliness of the incoming raw materials and the specific type of polymers being processed. This in turn will depend upon the efficiency of the sorting and pre-treatments of the incoming polymer waste stream. The emission of undesirable fumes will also depend on the correct process control. The level of fume production will again vary with the type of plastic that is being processed and even the formulation of each specific individual polymer. It will also depend on the operating conditions, including the correct use of recommended temperatures, dwell times and other key treatment procedures such as cleaning, purging, reliable temperature control and proper equipment maintenance.

Process operators will need to be made aware of these potential issues and provided with protection against such undesirable emissions. This might be achievable via the correct installation of localised exhaust and ventilation systems, coupled with an appropriate and optimised design of the overall recycling facility. Ultimately, in many cases, it will be necessary for individuals to be provided with appropriate personal protection equipment (PPE). General good advice for those engaged in plastic recycling includes;

- Perform recycling in a well-ventilated space or a ventilation system
- Wear an appropriate mask appropriate for the polymer type being recycled, even when working in a well-ventilated space
- Ensure that the plastic being processed is properly cleaned before exposure to elevated temperatures, e.g. when melting, as some residues can result in the release of harmful fumes
- Separate individual polymer types whenever possible to avoid materials with different melting points being processed at the same time
- Avoid overheating, use the lowest possible temperatures for the shortest time to avoid polymer degradation and generation of volatile decomposition products
- Wear heat resistant gloves when operating heated machinery

More importantly, any company carrying out plastic recycling should undertake a proper risk assessment of the whole process, especially as it is likely that workers actually operating the various pieces of equipment etc are likely to be undertaking tasks that can expose them to risk e.g. using the equipment, machinery and chemicals. It is thus important to carefully consider each individual task or operation in order to determine the following;

- who might be affected
- how they might be harmed
- what measures are currently in place to prevent this type of harm
- whether the measures are sufficient to stop people being harmed

This process is the basis of a risk assessment, which should not only be performed for the whole process, but recorded in such a way that it can be used to prevent harm to process operators.

At the time of writing, the specific process stages and operating details of the Sol-Rec2 process were still being developed. Additionally, it is already clear that, given the disparate nature of the incoming materials needing to be processed, there is unlikely to be one single process. Rather there will be processing variations where individual stages may be changed, added or removed. Currently, the process focus is on waste food packaging and medicine blister packs. Within food packaging, there are many different combinations of materials in use, each of which will require varying process parameters. Similarly, medicine blister packs often utilise PVC and it will be very important to ensure that it is possible to segregate such packs from non-PVC types. Even the condition of the incoming raw materials will impact the process; there is likely to be a need for careful sorting followed by washing and drying stages in the early part of the process in order to remove food and medicine residues. Conversely, if the incoming materials can be of guaranteed cleanliness, it might be possible to avoid these process stages, although this seems unlikely, as it would severely limit the amount of material that could be recycled. Similarly, there will be a need for comminution stages and their associated equipment e.g. shredders and granulators.

The work carried out to date on the use of ionic liquids/deep eutectic solvents to separate the individual components of the packaging has indicated that a pre-treatment comminution stage is beneficial. By shredding the input materials to a particle size of between 4 and 6 millimetres, separation can be achieved in just a few minutes at temperatures between 70 and 80 ºC using an appropriate low-cost ionic liquid. The separation is likely to be achieved using ionic liquids based on aliphatic acids such as ethanoic acid and an appropriate amine. Following separation of the components they will need to be individually isolated and recovered as dry solids, so that they can be further processed as required and so the ionic liquids can be recycled in a closed loop approach for further use. How this will be achieved is not yet clear, but it will require some type of filtration, possibly using a filter press, for example. Each of these process stages will have environmental, health and safety aspects that must be considered in order to ensure operator safety and to eliminate any undesirable emissions or waste generation.

The basic potential stages of the generic Sol-Rec 2 process are outlined in the table below.

Process Stages	Activities	Key Considerations
Packaging waste delivered for treatment	Initial sorting to remove any packs that are not empty/ contaminated. Sort by type of polymers used.	Mechanical/manual process to ensure there is no contamination. Separate PVC from non-PVC. Can digital water marks be used?
Shredding of input material	Use a shredder to produce particles within the 4 to 6 mm range.	Smaller particle size facilitates more rapid separation of component materials. Safety and energy consumption. Formation of dust.
Washing	Removal of contaminants, eg residual food, dirt and possibly some unused medicines.	Depends on the quality of the incoming materials. Should this be before shredding as well as afterwards? Treatment and disposal of contaminated washings, will add a cost and generate waste. Recycle and reuse water in a closed loop process.
Material separation	Process to remove lid material e.g., aluminium and to separate individual plastics, adhesives, inks etc.	Uses ionic liquids and heat (70-80 ºC) to separate various components of the packs. Produces polymer, metal and adhesives.
Filtration and other treatment to produce individual insoluble materials	Solids i.e., materials such as aluminium, polymer (PP, PET & PVC) and adhesives separated from the ionic liquid.	This will result in pure polymer and metal fractions plus the ionic liquid that can be recovered and reused. Need to consider the loss of ionic liquid/residual amounts in the recovered materials.
Further treatment of precipitated polymer as required for new applications	Use of established processes to formulate polymers and tailor final properties for specific second life applications.	Mainly mechanical processing that could include compounding, milling extrusion and granulation.

Table 1: Basic overview of the generic Sol-Rec2 process stages

3.2 Mechanical Aspects of the Sol-Rec2 Process

3.2.1 Introduction

The Sol-Rec2 process has a focus on the packaging used for food and medicines which typically comprise multiple layers of disparate materials. The processing of these materials requires a series of both mechanical and chemical stages each of which may be manual, part automated or fully automatic. During the early stages after delivery to the processing plant, the initial processing will involve activities such as washing/cleaning to remove any residual food and drugs as well as any other undesirable substances such dirt. There will thus be individual sorting and cleaning steps which could involve a degree of manual intervention and thus the possibility of exposing operators to health and safety related issues. Depending on the scale of the operation, the size of the facility and the condition and way that the incoming waste packaging is delivered and stored, it is likely that large quantities of these baled input materials will routinely need to be moved from the initial storage area to where they are subsequently processed.

In conventional recycling plants, these movements will be conducted by forklift trucks that deliver the input materials to an integrated transport system such as a conveyor belt which further moves the material for subsequent mechanical activities such as additional sorting or perhaps directly to washing or various types of comminution processes i.e., grinding and shredding. These are predominantly mechanical process and each has its own distinct potential health and safety aspects that can impact operators. It is also worth noting that in many recycling facilities, sorting is also conducted manually. Irrespective of whether this sorting is conducted automatically or manually, the main objective is to produce the purest possible input materials. Sorting is thus also likely to be a source of waste materials whose disposal needs to be carefully executed in order to avoid subsequent negative environmental impacts and additional disposal costs. If the separation and sorting is to be conducted mainly manually, it is important for the health and safety of the operators that the sorting area is provided with good ventilation.

Although, at the time of writing, the Sol-Rec2 pre-treatment stage requirements were still to be defined, it is clear that some type of comminution activity will be required such as shredding and grinding, along with any other pre-treatment stages. These operations typically require the use of powerful machines and trained operators. The workers typically monitor the process to ensure that no malfunctions occur and they also maintain and service the equipment. The machinery used can often be noisy (although more modern units tend to be somewhat quieter) and also generate dust etc, so it is important to ensure that the operators are provided with appropriate protective equipment. If the average noise exposure levels are 85 decibels or above, the provision of hearing protection is mandatory; at 80 decibels it must be made available; but below that it isn't required.

In some established plastic recycling facilities, washing of the materials takes place after these comminution stages. The shredded materials are cleaned in large washing baths where any unwanted contaminants on the surface are removed. Again, this type of approach often requires manual interventions, such as skimming off any floating substances from the surface of the washing bath. Once washed, the clean materials can be dried and made ready for the next stage of processing. Washing and the treatment of the waste water generated is covered in more detail in a separate section below. In the case of the Sol-Rec2 process, this may be the material separation stages where task specific ionic liquids are used to separate the individual components of the packaging. While this is essentially a chemical dissolution process, there is also likely to be an appreciable mechanical contribution, perhaps with a degree of manual intervention or the use of ultrasonics. In addition to loading of the materials, if a batch process is used, there are also likely to be heating, cooling, precipitation and stirring activities. The intention here is to separate the valuable polymer fractions and aluminium that can subsequently be recycled. In the case of the polymers recovered, they will subsequently be used with formulation aids and other additives to produce recyclate materials with properties tailored for specific applications. Whether these activities are specifically part of the overall Sol-Rec2 process, or are perhaps performed elsewhere, remains to be seen. If an integrated plant approach appears to be the best way of recycling the key materials, then there will be a range of subsequent mechanical treatment stages following separation and purification of the key polymer components. These will each have their own EH&S requirements that will need to be considered.

The subsequent re-formulation of the individual recovered polymer types requires them to be melted and mixed with a range of different additives to tailor their properties for specific applications, or even just to enable further processing to be carried out. Typical additives include pigments to give a required colour in the subsequent product, although there are many other types of additives that are also likely to be used. They are typically mixed with the polymer using a variety of continuous flow systems, with the additives being dosed automatically. While these processes are largely automated, they do require the input of skilled operators who monitor them and ensure that the materials are loaded into and output from the machines correctly. In some cases, the additives may be partly loaded into hoppers by hand from containers. As the operators are thus in close proximity to the machinery, there is the potential for exposure to high temperature molten polymers, as well as fumes emanating from the equipment. It is good practice to prevent accidental contact with any parts of the equipment that are hotter than 80 °C via the use of guards or insulation. Where hot parts have to be exposed, appropriate warning signs should be in place. Operators should also be equipped with personal protective equipment and the processing should be performed in a well-ventilated area.

The molten compounded materials are subsequently extruded whereby the ground plastic fraction is passed through an extrusion barrel with screws at elevated temperatures. At the output end the continuously flowing material is chopped into a granulate with the requisite properties. There is thus the potential for exposure to hot molten material, especially during start-up of the equipment. Where possible, splash guards should be put in place. This typically represents the end the recycling process. During the extrusion part of the process the operators have to ensure the reliable continuous operation of the equipment. There is a level of ongoing machine maintenance and cleaning needed with various components needing routine removal and replacement. It is important, therefore, to provide protection against trap hazards. These can occur at various locations including openings in the barrel and when accessing the extruder screws. Direct access to the rotating screws should be prevented via the use of guards, grills and appropriate safety interlocks.

It is also the case that a significant number of extruder accidents occur during the changing of dies and while purging, so it is thus very important to have well documented safe systems of work.

If an extruder overheats, the plastic being processed may start to degrade, leading to the emission of undesirable vapours. In the case of PVC and other chlorine-containing polymers, this can result in chlorine-bearing compounds (such as HCl) being released. Operators will need to be made aware of this possibility and be provided with suitable protective equipment. The health and safety aspects of PVC recycling are covered in more detail in a following section.

3.2.2 Shredding

The incoming material supplies for the Sol-Rec2 process are likely to be bales of mixed plastics in the same physical form as when they were discarded, i.e. large pieces of packaging comprising multiple materials and, most likely, with some level of contamination as well. Before they can be treated in the Sol-Rec2 material separation process, there will need to be some pre-treatment and this will include processing to reduce the particle size to that which is optimal for the ionic liquids used to operate most efficiently. This size reduction will be achieved via the use of a shredding operation, a process stage that is commonly used by plastics recyclers. It is thus well understood and a convenient way of converting plastic waste into granules suitable for further processing. Nevertheless, there are a number of important health and safety aspects that need to be understood, and various measures must be implemented if this part of the process is to be utilised in a manner that avoids presenting risks to the operators. There are also, although to a less significant degree, potential environmental risks that need to be understood, if the process is to avoid having wider detrimental impacts. At the heart of a shredder there will be a series of rotating blades that are used to reduce the size of the plastic waste. Typical examples are shown in the figure below.

Examples of the types of blades used for shredding plastic waste.

These often rotate at high speed. There are clearly potential health and safety issues around the operation of shredders, especially as they are often sizeable pieces of powerful equipment. It is, therefore, essential that operators using a shredder are properly trained and know how to work in a safe manner, as misuse can lead to serious injuries and even death. Training is also required to meet insurance requirements. The specific training required will vary with the type and scale of the equipment, but it should cover the basic fundamentals of the machine, its operation and its functionality. Modern shredders are typically equipped with a range of integrated safety features and devices and these should be highlighted along with the basic checks that must be carried out prior to operation. Nevertheless, there are numerous potential hazards associated with their operation and these include;

- Contact with the shredder blades and knives – power to the blades must be provided via interlocked circuits to ensure they are unable to move until all guards are closed
- Entanglement with moving parts of the equipment (e.g. during routine maintenance, cleaning and repair operations)
- Impact from ejected plastic pieces – flexible curtains can be employed to minimise this risk and operators should wear face protection
- Dust – this can lead to both eye irritation and breathing problems, so plastic dust must be contained as much as possible during granulation. Respirators may also need to be worn. Excessive dust can be a significant contributor to explosion

- The possibility of fire and explosion within the equipment – it is important to have fire extinguishers readily available and to ensure operators are trained in their use. There should also be appropriately placed detectors and use could be made of sprinklers
- Slips, trips, and falls – many slips occur due to floors contaminated by water, fluids, waste plastic film, or spilled resin beads and granules. The area around the unit should be kept clear of anything that could cause such problems
- Collision between moving and fixed blades/knives – this can be avoided by ensuring that the blades are properly fitted and adjusted according to the manufacturer's instructions.

Shredders can also generate a significant amount of noise and it is thus important that operators are provided with appropriate hearing protection in order to prevent hearing damage or loss. This, of course, is in addition to the other PPE that will be need to be provided to operators, i.e. dust masks, safety glasses, gloves, face protection, overalls, high visibility jackets and safety boots/footwear.

The UK's Health and Safety Executive has produced a useful short document entitled 'Safety at Granulators' and it gives practical advice for owners and users of granulators. It also provides information on the commonly accepted and practicable safeguards for significant hazards on granulators.

3.2.3 PVC Recycling

Medicine blister packs often utilise poly vinyl chloride (PVC) or polyvinylidene chloride (PVDC) as one of their main components and thus these halogenated materials will be processed by the Sol-Rec2 process. Whether it will be possible to separate PVC and PVDC by sorting during the early stages of the recycling process remains to be seen, but it might be possible to do so if the project's digital watermarking technology is adopted by the blister pack manufacturers. However, it is clear that there will be a need to process chlorine-containing polymers through a number of mechanical and chemical process stages in order to produce a useable recyclate material. In recent years, there has been a lot of concern about the hazardous nature of chlorinated polymers such as PVC at end of life, but it is generally accepted that recycling is the preferred end of life treatment. It is also worth noting that the PVC formulations found in medicine blister packs do not usually contain the types of more toxic and hazardous additive materials found in PVC formulations used in other applications. Examples here would include the lead and cadmium-based stabilisers which have been phased out, but which can still appear in legacy products such as older window frames. More recently developed stabilisers are typically based on less hazardous materials such as tin, calcium, barium and zinc.

PVC is currently recycled in one of two ways, i.e. by mechanical or chemical processing. Mechanical processing typically involves mechanical comminution of the waste product to produce a granulate material. In mechanical recycling, the recyclate retains its original composition and the resulting granules can then be reused to make similar products from which the source material was obtained. Alternatively, the PVC can be subjected to chemical degradation processes such as pyrolysis, hydrolysis and heating that ultimately breakdown the PVC into its chemical constituents. The resulting products can then be used to produce new PVC, or as fuel to recover the embodied energy.

In the Sol-Rec2 process, there will be multiple treatment stages and these will be both mechanical and chemical. Mechanical processing will be used initially to reduce the size of the materials and to give a large surface area that will be more susceptible to subsequent chemical treatment. This treatment will separate the PVC from the other multilayer components and, possibly, also isolate the pure PVC from these as well as from its own formulation additives (if present). From a health and safety perspective, there are thus a number of considerations specific to the process steps. In the mechanical stages there will be the possibility of exposure to dust and fine particles while the materials are being shredded. There may also be mechanical stages after the chemical separation where the recovered pure PVC is reformulated and processed into material suitable for new applications. These may include extrusion at elevated temperatures, where there is the possibility of fume generation and thus exposure to toxic chemicals such as hydrogen chloride. PVC decomposes readily when overheated, as well as when subjected to excessive shear. Decomposition is reported to become apparent at temperatures as low as 135 °C and it spreads quickly because the hydrogen chloride (HCl) generated catalyses further degradation. HCl attacks metals such as steel, while also being very harmful to human beings.

The chemical stages of the Sol-Rec2 process will primarily cover the separation and isolation of the individual ingredients including PVC, which should then be relatively pure. The main hazards associated with this part of the process will be associated with the other materials used, e.g. components of the ionic liquids, and these will be covered in detail in the following section.

3.3 Chemical Aspects of the Sol-Rec2 Process

3.3.1 Introduction

The Sol-Rec2 process has multiple stages some of which are mechanical and some that use chemicals. The key innovative part of the overall process is the use of specific ionic liquids to separate the various material layers found in multilayer food and medicine packaging. This is clearly a chemical-based process and requires the use of specific tailored materials. The other part of the process where chemicals are used is in the washing stages that clean the incoming waste raw materials. These essentially involve the use of water, probably both before and after shredding, but chemical additives will be also be used to improve the separation achievable using ionic liquids and to help reduce the operating temperatures.

From a health and safety perspective, the biggest issue is likely to be with the individual chemicals used to form the specific required ionic liquid. There is also likely to be a need to employ other chemical additives when reformulating the recycled polymers in order to tailor their properties for specific applications. These formulation aids are typically necessary to help ameliorate the degradation in key properties that often occurs when the polymers being recycled are exposed to high temperatures.

Whenever chemicals are used, it is important to perform a Control of Substances Hazardous to Health (COSHH) assessment. These assessments will need to review how the chemicals are used and stored in the recycling facility. In particular, a COSHH assessment will determine how operators could be exposed to the chemicals such as via skin absorption or inhalation and what harmful effects such exposure could have.

This section therefore has a focus on these three chemical related aspects of the recycling process.

3.3.2 Ionic Liquids – Environmental, Health and Safety Considerations

Ionic liquids (IL) are often cited as being more environmentally friendly, less hazardous alternatives to many of the common solvents used in a wide range of chemical processing applications. In particular, their low vapour pressures, and thus comparatively low volatilities, mean that they are considered to be a safer choice. They do not evaporate into the atmosphere where they could contribute to smog formation, ozone depletion, and climate change. While this lack of volatility reduces the likely impacts of their accidental release on the environment, it is also important to understand that they can still be toxic. In some cases, they may even be more toxic than the traditional solvents they replace. Another often cited advantage associated with their low vapour pressures is the lack of flammability compared to conventional solvents. However, just because some ionic liquids are not themselves flammable, it does not mean that they are safe to use in close proximity to open flames and heat sources. A large group of ILs are actually combustible due to the nature of their positive heats of formation, oxygen contents, and decomposition products.

Because there is such a wide range of ionic liquids available with markedly different chemical structures, they also exhibit a wide range of properties. For example, some are approved for food use, while others are toxic. As they can exhibit good water solubilities, ILs can easily find their way into the aquatic environment, which then presents a potential threat to the aquatic environment itself and the organisms living there. Additionally, ILs may have high stabilities that make them poorly biodegradable, meaning that they can persist in this environment for a substantial period of time.

It is important to understand the properties of each individual IL when making an assessment of the environmental, health and safety aspects needed of a specific material. For example, an understanding of an ionic liquid's chemical stability as a function of the temperatures likely to be experienced in a particular process stage is very important. Also, because the Sol-Rec2 process has multiple steps, it is also important to understand how an IL will behave in the presence of other materials, especially solvents and water. Such knowledge is not only vital when making selection decisions for specific applications, but also to ensure that there are properly derived safe handling procedures. For example, it is known that alkyl sulfate-based ILs hydrolyse in the presence of water as a function of temperature. Their stabilities depend on the alkyl chain length of the anion with methyl and ethyl sulfate-based ionic liquids being unstable in the presence of water, while the larger alkyl sulfate based ionic liquids only start to decompose when exposed to much harsher conditions.

The ionic liquids currently under initial investigation for use in the Sol-Rec2 are listed in the table below. This shows the constituent chemicals and any EH&S considerations that need to be considered. The key issues are likely to be associated with the organic acids used to produce the DESs and the fact that the process operates at 70 ºC. For advice on best practice when using materials such as acetic (ethanoic) acid, reference should be made to the Materials Safety Data Sheets that are available from the chemical supply companies. Sources of relevant MSDS's are provided in the appendix at the end of this document.

Material	Constituents	Operating Temperature	EH&S Concerns	Other Comments/Issues
DES1	Thymol Acetic acid	70 ºC	Thymol, glacial acetic acid	Wear suitable PPE when handling chemicals. Wear suitable respiratory equipment if handling the chemicals in an area that isn't well-ventilated.
DES2	Betaine Acetic acid	70 ºC	glacial acetic acid	Wear suitable PPE when handling chemicals. Wear suitable respiratory equipment if handling the chemicals in an area that isn't well-ventilated.
DES3	Thymol Propionic acid	70 ºC	Thymol, propionic acid	Wear suitable PPE when handling chemicals. Wear suitable respiratory equipment if handling the chemicals in an area that isn't well-ventilated.
DES4	Betaine Propionic acid	70 ºC	Propionic acid	Wear suitable PPE when handling chemicals. Wear suitable respiratory equipment if handling the chemicals in an area that isn't well-ventilated.
IL	Amine+Organic acid	40-70 °C		Wear suitable PPE when handling chemicals. Handle IL precursors under a fume hood. Wear suitable respiratory equipment if handling the chemicals and final IL in an area that isn't well-ventilated.
Cleaning Solvent/Waste	Contaminated water	Room Temp.	Decontaminating	Wear suitable PPE when handling chemicals.
Cleaning Solvent/Waste	Ethanol/Acetone	Room Temp.	Recycling	Wear suitable PPE when handling chemicals.
Solvent/Waste	Any organic solvent used to rinse the delaminated sample from wet IL/DES (EtOH might be a good candidate)	Room Temp.	Recycling	Wear suitable PPE when handling chemicals.

Initial list of deep eutectic solvents and related chemicals identified by the University of Leicester and Solvionic that may be used in the Sol-Rec2 process

The following amines and acids are all potential components of the deep eutectic solvents that could be used in the Sol-Rec2 process.

- **Amines:** 1-methylimidazole (CAS 616-47-7), 1-ethylimidazole (CAS 7098-07-9), Pyridine (CAS 110-86-1), 4-methylpiperidine (CAS 626-58-4), N,N-dimethylbenzylamine (CAS 103-83-3), trioctylamine (CAS 1116-76-3), N-methylmorpholine (CAS 109-02-4).
- **Acids:** acetic acid (ethanoic acid) (CAS 64-19-7), propanoic acid (CAS 79-09-4), butanoic acid (CAS 107-92-6) and decanoic acid (CAS 334-48-5)

While these individual amines and acids may each have their own specific health and safety requirements when handled in isolation, once used in combination to form the requisite ionic liquid/deep eutectic solvent their volatilities and toxicities are likely to be significantly reduced, or even eliminated. (Consider, for example, Solvionic's PYR13FSI, which comprises an N-Methyl-N-propylpyrrolidinium cation and a Bis(fluorosulfonyl)imide anion and that has achieved REACH conformity).

In terms of the actual Sol-Rec2 process itself, the use of ultrasonication which could lead to noisy working conditions for operators is an additional EH&S consideration that must be considered. Depending on the size, power and location of the ultrasonic transducers used, it may necessary to provide operators with hearing protection. It should also be noted that some of the precursor materials listed above for the deep eutectic solvents and ionic liquids may have unpleasant smells, even at very low ppm levels.

3.3.3 Water and Washing

With many plastic recycling processes the cleanliness of the incoming feedstock is critical in determining the quality and hence the value of the recyclate produced. The higher the quality of the output material, the more likely a recycling process itself will be economically viable. In the Sol-Rec2 process, the intention is to produce very high-quality materials that have not been degraded either chemically or thermally. Given then, that the feedstock materials likely to enter the Sol-Rec2 process may, in all probability, contain residual food and medicines contaminants, there will be a need to ensure that such contamination is effectively removed prior to processing. This will require some form of manual or automated sorting, but will also involve washing. Washing of incoming raw materials is often a critical component in many polymer recycling processes, as it plays a key role in determining the quality of the output recyclate. The actual level of washing and the type of approach adopted can have a significant impact on the overall energy and resource consumption of a recycling plant. Furthermore, there are important environmental considerations, as the contaminated washing effluent can cause wider problems without appropriate treatment.

Although the washing operations required vary with each specific recycling process, it is often necessary to implement more than one washing stage. It is also advantageous to employ cleaning agents in the water and various manufacturers supply chemical formulations specifically developed for plastic recycling. They are aimed at helping to optimise the efficiency of the washing process while also being amenable to appropriate waste water treatment processes. These additives typically include cleaners, defoamers, and wetting agents. An example showing where washing is used in a PET recycling operation, and the types of additives used, is shown in the figure below.

Clearly, the washing stages will each produce contaminated water that will need to be subjected to an appropriate treatment process, so that the water can be reused via a closed loop process in further washing cycles or, alternatively, safely discharged. During this part of the process, it would again be typical to use various flocculants and coagulating agents.

By carefully selecting the appropriate additives, it is possible to achieve enhanced cleaning efficiencies at lower temperatures, thus reducing energy consumption, while minimising any harmful environmental impacts.

Incoming material for recycling

Prewashing (cleaners and defoamers)

Grinding/Shredding

Washing (cleaners and defoamers)

Floatation/Separation (wetting agents and defoamers)

Rinsing (defoamers)

While the general washing requirements for producing good quality recyclate are reasonably well understood, various recycling machinery manufacturers have developed their own specific approaches. For example, the equipment produced by the German company, B+B Anlagenbau GmbH takes shredded contaminated plastic waste material into its washing line where it is first conveyed through a cold-water friction washer for removing light contaminants. After this initial wash, the next step involves drying the material stream and separating further contaminants. This is performed in a mechanical dryer. For highly contaminated material, such as the removal of adhesives from labels, and to meet food grade standards, a second washing stage can be utilised. In a continuous hot washer, the flakes are soaked in a mixture of hot water washing solution, followed by a friction washer where the material is rinsed. In a subsequent sink-float tank, different types of polymer flakes scan be separated e.g. PET from PE/PP from bottle caps. Finally, a mechanical dryer will dewater the PET flakes while the polyolefins are dried by a thermal dryer.

The above is just one example of a washing process used for cleaning incoming waste plastic. At the time of writing, it is not yet clear exactly what level of cleaning will be needed prior to the separation stage of the Sol-Rec2 process. However, washing is an important component of the Sol-Rec2 process and it will need to be optimised in order to reduce the amount of waste water generated, to maximise the amount that can be recycled and reused, and to minimise any additional costs and subsequent negative environmental impacts.

3.3.4 Additives for Maintaining Recyclate Performance

When polymers are recycled, they often need to have their properties modified or enhanced with additives. This can typically be to help improve key properties that have been degraded during the recycling processing, but it can also be in order to help mask or eliminate undesirable odours than can be emitted by some recycled plastics, especially those that have been in contact with food. It is well known that certain undesirable species can be generated in plastics during recycling. For example, increased levels of acetaldehyde are often produced when PET is recycled. This in turn can lead to food items packaged in recycled PET containers having an 'off'-taste. There are many types of chemical additives that may need to be used and some of the common types are as follows;

- plasticisers — examples include low volatility esters
- antioxidants — various organic chemicals that protect against thermal decomposition during processing
- stabilisers — both inorganic and organic chemicals that provide protection against thermal decomposition and UV degradation
- lubricants
- fillers — typically low-cost inorganic materials used to impart required properties (e.g. lowering thermal expansion) or to reduce cost.
- colourants — both inorganic and organic compounds to provide required colour
- blowing agents — materials that emit gases to produce plastic foams.

From a broad EH&S perspective, there is thus the challenge of producing a recyclate that is itself safe for use in the subsequent applications for which it has been formulated. This has been particularly problematic when recycling plastics for reuse in food contact material applications. In order to ensure consumer safety, the European Food Standards Agency (EFSA) requires that recycled food-grade materials can only be made from >95 % food packaging and that the recycled plastic must meet the same high standards required for virgin food-grade plastics. There is strict and comprehensive legislation that specifically addresses the use of recycled plastics in food contact applications. A good example is the European Commission's Regulation (EC) No 282/2008 on recycled plastic materials and articles intended to come into contact with foods.

From the perspective of the Sol-Rec2 process, there are thus a number of potential EH&S related considerations. Firstly, the process itself must be able to generate high value recyclate that can be used in wide range of applications. Given that the incoming raw material is likely to have some contamination and that the subsequent processing involves both chemical and mechanical/thermal treatment stages, it is essential that the final output product is not degraded, or contaminated in any way. As ionic liquids have low vapour pressures, it may be a challenge to ensure that residual amounts are not present in the recyclates produced. If they are not fully removed, they could have EH&S implications for those both processing and using the recyclate.

To enhance the final properties, it is common practice to introduce any of a number of additives when processing and reformulating recycled polymers. Examples of the reasons why this may be necessary are mentioned above. However, it will be important that operators are aware of any handling pre-cautions that are necessary for each type of additive, as there are a potential health hazards associated with the processing of plastics. When reformulating recycled plastics via the use of additives, appropriate precautions must be taken specific to each type of additive used in the various formulations. For example, there can be a significant risk of dermatitis from some types of reactive liquid and powder additives. Operators should thus be provided with, and required to wear, appropriate personal protective equipment.

It will also be important from an EH&S perspective to ensure that any additives selected are suitable for the specific application intended for the recyclate and that they do not compromise the use of the material in certain applications. Operators must also be made fully aware of any health and safety issues associated with each particular additive type, so that appropriate protection can be used.

4 Sol-Rec2 – Risk Assessment and Minimisation – Pilot Plants

4.1 Introduction

Whilst the risk assessment and associated minimisation demand are as set down in detail in this section and are as defined by hazard and operability study (HAZOP) procedures, it should be noted that such is comprehensive and very detailed. This is because it is directed towards the design and operational study of a pilot plant to be constructed and operated within a manufacturing or simulated manufacturing environment. Thus, it is sufficiently detailed to embrace a pilot plant which is to be utilised primarily for the identification and optimisation of all procedures relevant to those within a full-scale manufacturing environment.

In terms of the risk assessment and minimisation pertinent to the Sol-Rec2 project, it should be borne in mind that the plant to be designed, constructed, installed, commissioned and operated for the defined process can best defined as a large-scale laboratory model, i.e. a comparatively small pilot plant. As such, it will be operated by highly skilled and qualified technical, scientific and engineering personnel. Its principal objectives will be more appropriate to those associated with a process feasibility study. This smaller scale does not imply any by-passing of procedural necessities, but simply reflects the key elements that need to addressed within a risk-based study considering the location and scale of the equipment, the staff operating the equipment and the operational objectives looking to be realised, which in essence are relatively short term.

Accordingly, a somewhat curtailed HAZOP study tailored to the laboratory-scale pilot plant destined for Sol-Rec2 studies should embrace the following aspects:

- Plant Design – in respect of materials of construction, the operational criteria such will be subject to (temperature, chemicals, pressure etc) and perceived hazard and environmental assessments taking input from all collaborators.
- Plant location and layout – proximity to utilities such as power, water, air, extraction, space requirements and screening as deemed necessary.
- Operating procedures via a written and electronically accessible manual covering all operational aspects and appropriate issued documentation such as MSDSs for applied chemicals and OEM literature for plant elements such as pumps, dosing and monitoring equipment etc.
- Installation and commissioning should be via an issued and approved method statement.
- Start-up, shut down and emergency procedures for all aspects should be via a clearly visible printed documented sited adjacent to the equipment.
- A training module for all staff using the equipment should be implemented.

The scale-up of a laboratory chemical process to a larger pilot plant stage places demands on minimising the risks associated with the proposed plant, the process, the plant design, commissioning, operation and maintenance. Therefore, it is recommended that any further scale up of the Sol-Rec2 pilot plant towards a larger manufacturing plant size should be subject to a much more substantial HAZOP study. The prime objective of HAZOP is the identification of problems. The following detailed documentation about the requisite HAZOP approach and methodology is based on documentation originally produced by Johnson Matthey. This was for a similar pilot plant developed in an earlier project, that was also focussed on valuable material recycling and recovery. Much of the detailed information was derived from very apposite and useful documentation about pilot plants that has been produced by the UK's Health and Safety Executive (HSE). The authors therefore acknowledge the contribution to the following section made by Johnson Matthey and the UK HSE.

The concept and the essential stages/elements relating to pilot plants are outlined in Section 1. This is followed by the key measures recommended to ensure total HAZOP conformity, and these are detailed in Section 2. Section 3 provides details of the more specific potential risks associated with each of the identified potential Sol-Rec2 process stages.

Section 1 – Hazard and Operability (HAZOP)

Introduction to HAZOP

A hazard and operability study (HAZOP) is based on the principle that several experts with different backgrounds can interact and identify more problems when working together than when working separately and combining their results. The HAZOP concept is to review the plant in a series of meetings, during which a multidisciplinary team methodically 'brainstorms' the plant design, following a structure based on specific aspects of the pilot plant design.

A hazard and operability (HAZOP) study is a design review technique used for hazard identification, and for the identification of design deficiencies which may give rise to operability problems. HAZOP is most commonly applied to systems which transfer or process hazardous substances, or activities where the operations involved can be hazardous and the consequences of failure to control hazards may be significant in terms of damage to life, the environment or property. A HAZOP study is carried out using a structured approach by an experienced multi-discipline team. The key activities are to;

- Identify hazards and operability issues associated with the design
- Identify deviations from design intent, deviation causes, consequences, and safeguards
- Provide an action list with due dates and identify appropriate person/discipline to progress the action to close out

In the instances put forward for Sol-Rec2, a suggested HAZOP study structure would cover input into situations likely to result in a hazardous outcome by a line-by-line analysis of the design PID diagrammatic or a study covering the following overview issues:

- first start-up procedures
- emergency shutdown procedures
- alarms and instrumentation trip testing
- pre-commissioning operator training
- plant protection systems
- failure of services
- breakdowns• effluent (gas, liquid, solid)
- noise.

Any issues raised and considered necessary for review outside the HAZOP should be detailed.

Actions arising from HAZOP should identify those actions or activities which are potentially hazardous to plant personnel, the public or the environment. This should be followed by a clear commitment to modify the design or operational procedures in accordance with the identified required actions.

It should be noted that it may be deemed somewhat more appropriate to conduct a HAZID (hazard identification) study as opposed to a HAZOP one which is considered to have greater application at the design or conceptual stage of the pilot plant. Early identification and assessment of hazards provides essential input to project development decisions at a time when a change of design has a minimal cost penalty. A HAZID study is carried out by an experienced multi-disciplinary team using a structured approach based on a checklist of potential hazards. Potential problems are highlighted for action outside the meeting. Typical process hazards are considered such as environmental, geographical, process, fire and explosion. HAZID objectives may be set down as:

- Identify hazards to the host facilities due to design, and evaluate potential consequences should the hazards be realized
- Establish safeguards to manage hazards; identify areas where further understanding of safeguard effectiveness is needed
- Make recommendations to reduce the likelihood of hazard occurrence or mitigate the potential consequences.

The detailed measures covered in Section II of this report embrace all of the steps that, if incorporated, would address any perceived issues from a HAZOP study.

4.2 Section 2 – Measures to ensure HAZOP conformity and to mitigate risk of any major incident involving chemical processes.

Introduction

Within the Sol-Rec2 project, there are potentially a number of chemical processes appearing to display viability of approach in chemical leaching and recovery of plastics from used or redundant multilayer packaging. It is proposed to further assess the viability of each these processes by scaling up from a laboratory model to an operational pilot plant.

Irrespective of the individual chemical process deployed, there are many general principles and procedures which should be followed in the pursuit of the elimination or minimisation and control of potential risks and hazards which may in turn result in an accident.

The following is intended to cover procedures relating to maintenance, control systems, training, containment and emergency response/spill control which should form the basis of ensuring that the pilot plant design and active parameters are commensurate with the minimisation of risk. Whilst what is set down is a comprehensive procedural risk minimisation level of documentation for chemical process plant and pilot plant, the relatively small scale and simplicity of the proposed Sol-Rec2 plant should necessitate only an awareness of these factors.

Plant Design

The design of a process plant is a complex activity that will usually involve many different disciplines over a considerable period of time. The design may also go through many iterative stages from the original research and development phases, through conceptual design, detailed process design and onto detailed engineering design and equipment selection. Many varied and complex factors including safety, health, the environment, economic and technical issues may have to be considered before the design is finalised.

At each stage, it is important that the personnel involved have the correct combination of technical competencies and experience in order to ensure that all aspects of the design process are being adequately addressed. Evidence of the qualifications, experience and training of people involved in design activities should be presented in the Safety Report to demonstrate that the complex issues associated with the design have been considered and a rigorous approach has been adopted.

The process design will often be an iterative with many different options being investigated and tested before a specific process is selected. In many instances, a number of different options may be available and final selection will then depend upon a range of factors.

The process design should identify the various operational deviations that may occur and any impurities that may be present. In the mechanical design, the materials chosen for construction need to be compatible with the process materials under both the standard operating conditions and certain excursion conditions. The materials of construction also need to be compatible with each other in terms of corrosion properties. Impurities which may cause corrosion, and the possibility of erosion also need to be considered so that the detailed mechanical design can ensure that sufficient strength is available and suitable materials are selected for the plant fabrication.

Detailed mechanical, structural, civil and electrical design of equipment comes after the initial process design, which covers the steps from the initial selection of the process to be used, through to the issuing of process flow sheets. Such flowsheets will include the selection, specification and chemical engineering design of the equipment. These are then used as the basis for the further detailed design.

This deliverable primarily considers the latter stages of the detailed design processes and identifies the detailed design issues, codes and applicable standards for the mechanical design of equipment.

Design factors are an essential component in order to give a margin of safety in the design. The design factors may be appropriate in either the mechanical engineering design or in the process design where factors are often added to allow some flexibility in process operation. For mechanical and structural design, the magnitude of design factors should allow for uncertainties in material properties, design methods, fabrication and operating loads. Plant design should take account of the relevant codes and standards. Conformity between projects can be achieved if standard designs are used whenever practicable.

Inherently Safer Design

The principles of inherently safer design are particularly important for major hazard plants and should be considered during the design stage. The Safety Report should adequately demonstrate that consideration has been given to the concepts. Some companies now have design procedures that require a review of designs and seek to ensure that inherently safer concepts have been addressed.

Inherently safe design should be considered during the design stage in an effort to reduce the hazard potential of the plant. Protective equipment installed onto standard equipment to control accidents and protect people from their consequences is often complex, expensive and requires regular testing and maintenance. Attempts should be made to reduce the requirement for such protective equipment by designing simpler and safer processes in the first instance. A number of approaches can be considered but, basically, an inherently safer plant can be achieved by minimising the inventories of hazardous substances in storage and in process. In this way the risk of a major accident can be significantly reduced.

Some of the techniques that can be considered are:

- Intensification - this technique involves reducing the inventory of hazardous materials to a level whereby it poses a reduced hazard. This often means carrying out the reaction or unit operation in a smaller volume. It can be applied to a wide range of unit operations including reactors, distillations and heat exchange, but it may involve different mechanisms and approaches having to be employed to the reaction chemistry and control systems;
- Substitution - this technique involves replacing a hazardous material (or feature) with a safer one. For example, flammable solvents, refrigerants and heat transfer media can often be replaced by non-flammable or less flammable (high boiling) materials. Often hazardous processes can also be replaced by inherently safer processes that do not involve the use of such hazardous substances or which operate at lower temperatures and pressures;
- Attenuation - using a hazardous material under less hazardous conditions. For example, quantities of chlorine, ammonia and LPG can be stored as refrigerated liquids under atmospheric pressure rather than under pressure at ambient temperature. Materials likely to form explosive dusts can be used and stored as slurries to minimise hazards;
- Limitation - affected by equipment design or changes to reaction conditions rather than by adding on protective equipment. For example, the selection of some types of gaskets can reduce leak rates from equipment in the event of a leak hence limiting the hazard. Many runaway reactions can be prevented, either by changing the order of addition, reducing the temperature or changing other parameters;
- Simplification - simpler plants are friendlier and safer than complex ones and therefore less likely to have a major accident caused by operator error;

- Knock-on effects - plants should be designed to reduce the likelihood of incidents producing knock-on effects or domino effects in other areas;
- Avoid incorrect assembly - for critical equipment plants can be designed so that incorrect assembly is difficult or impossible. Consideration should be given to installing different types of connections on inlet/outlet pipework to avoid the possibility of wrong connections being made.

General Design Considerations

There are several general topics that are common to the detailed mechanical design of many types of equipment and these are discussed in greater detail below:

- Temperature and Pressure;
- Materials of Construction;
- Corrosion/Erosion.

A number of potential hazards can be introduced if these are not given adequate consideration. Loss of containment may occur due to leaks, equipment failure, fire or explosion and result in a major accident.

Temperature and Pressure

Temperature and pressure are two basic design parameters. Any equipment that is to be installed should be designed to withstand the foreseeable temperature and pressure over the whole life of the plant. The combination of temperature and pressure should be considered, since this affects the mechanical integrity of any equipment that is installed.

Temperature

In determining design temperatures, a number of factors should be considered including:

- the temperature of the fluids to be handled;

- Joule-Thomson effect (The Joule-Thomson effect is the change in temperature that accompanies expansion of a gas without production of work or transfer of heat. At ordinary temperatures and pressures, all real gases except hydrogen and helium cool upon expansion and this phenomenon is often utilised in liquefying gases);
- ambient temperatures;
- solar radiation; and
- heating and cooling medium temperatures.

Consideration needs to be given to the temperature of the fluids that are to be handled and any excursions in temperature that could occur as a result of the failure of temperature control systems. Account should be taken of all foreseeable reactions that may occur that are likely to increase or reduce the heat input to the system.

The extremes of ambient temperature should be taken into account for plant situated outside buildings. Solar radiation on the exposed surfaces of large storage tanks can significantly increase surface temperatures for storage vessels leading to thermal expansion of the vessel contents. Likewise, the low temperatures that can be achieved under conditions of snow, ice and wind, which can cause solidification of contents in vessels and pipelines, should also be considered. External facilities should be designed to accommodate the cycling of temperatures between extreme weather conditions.

If secondary heating and cooling systems are employed then the maximum and minimum temperatures that can be achieved by these secondary systems should be assessed assuming failure of any control systems associated with these systems. Care should be taken to ensure the maximum temperature that can be achieved by heating oil systems or the minimum temperature that can be achieved by cryogenic cooling systems does not compromise the design of the equipment. It should not adversely affect the mechanical strength and hence integrity, or result in additional process hazards as a result of overheating, decomposition or runaway reactions.

The strength of materials decreases with increasing temperature and, therefore, the maximum design temperature should consider the strength of material used for fabrication.

Evidence should be provided in the safety report that the process conditions and environment in which the equipment is to be utilised have been assessed and that an appropriate design temperature has been selected.

Pressure

A vessel should be designed to withstand the maximum pressure to which it is likely to be subjected in operation. For vessels under internal pressure, the design pressure is usually taken as that at which the relief valve is set. This is normally 5 – 10 % above the normal working pressure in order to avoid inadvertent operation during minor process upsets. Vessels subjected to external pressure should be designed to resist the maximum differential pressure that is likely to occur. Vessels likely to be subjected to vacuum should be designed for full negative pressure of 1 bar unless fitted with an effective and reliable vacuum breaker device.

Account should also be taken of any foreseeable reactions which may occur that are likely to increase the heat input to a system, or gas evolution and hence result in increased or decreased temperatures and pressures. Where strongly exothermic reactions or runaway reactions are possible, it may not be possible to adequately design the equipment to withstand the maximum predicted temperature and pressure. Under such circumstances some form of pressure relief system may be appropriate in order to protect the equipment and prevent catastrophic failure from occurring. Pressure vessels should be fitted with some form of pressure relief device set at the design pressure of the equipment to relieve over-pressure in a controlled manner. The set pressure of a relief valve should be such that the valve opens when the pressure rise threatens the integrity of the vessel, but not when normal minor operating pressure deviations occur. It is necessary to balance a number of factors in the selection of relief valve set pressures since, if the potential cause of pressure rise is a runaway reaction, then setting the relief pressure at a high level above the normal operating pressure may allow the reaction to reach a higher temperature and to proceed more rapidly before venting starts.

During the operation of the relief valve the pressure at the inlet to the relief valve (the overpressure - this is usually taken to be no more than 10% for design purposes) can be expected to increase above the set point for the relief device. The accumulation in the vessel is the permitted increase in the system pressure above the design pressure in an emergency overpressure situation. The maximum allowable accumulated pressure (MAAP) is specified within the various codes and this should be considered when the relief valve set point is selected. Normally the relief valve set point is set below or up to the maximum design pressure which, allowing for the overpressure during a relief event, ensures that the overall pressure is below the MAPP.

Discharge of hazardous substances from relief systems under emergency conditions should be routed to secondary containment vessels, or to safe locations, so that additional hazards to personnel or equipment and the possible escalation of an incident does not occur. This should be considered as part of the mechanical design of the equipment if such systems are to be employed.

Evidence should be provided in the safety report that the process conditions and environment in which the equipment is to be utilised have been assessed and that an appropriate design pressure has been selected.

Consideration should be given to the possibility of pressure cycling in equipment and subsequent failure of the equipment due to metal fatigue.

Materials of Construction

Another important consideration in mechanical design is the selection of the material of construction. In some cases, the available materials of construction may constrain the design temperatures and pressures that can be achieved and limit the design of the equipment. The most important characteristics that should be considered when selecting a material of construction are summarised below:

- Mechanical Properties;
- Tensile strength;
- Stiffness;
- Toughness;
- Hardness;
- Fatigue resistance;
- Creep resistance;
- The effect of low and high temperatures on the mechanical properties;
- Corrosion resistance;
- Ease of fabrication;
- Special properties - electrical resistance, magnetic properties, thermal conductivity;
- Availability in standard sizes;
- Cost.

The selection of a suitable material of construction is often carried out by disciplines such as process engineers. The advice of specialist materials engineers should be sought in the event of difficult applications being identified.

Corrosion/Erosion

If materials to be used in the process are corrosive then this should be considered in the plant design and layout. Materials of construction should be carefully selected, protected where possible and regularly inspected if the presence of corrosive materials or a corrosive environment is anticipated.

The standard for pressure vessels recommends that all possible forms of corrosion such as chemical attack, rusting, erosion and high temperature oxidation are reviewed, that particular attention be paid to impurities and to fluid velocities, and that where doubt exists corrosion tests should be carried out.

The life of equipment subjected to corrosive environments can be increased by proper consideration of design details. Equipment should be allowed to drain freely and completely and the internal surfaces should be smooth and free from locations where corrosion products can accumulate. Fluid velocities should be high enough to prevent deposition but not so high as to cause erosion.

The corrosion allowance is the additional thickness of metal added to allow for material lost by corrosion and erosion or scaling. For carbon and low-alloy steels where severe corrosion is not expected a minimum allowance of 2 mm is often used, where more severe corrosion is anticipated an allowance of 4 mm is often used. Most design codes and standards specify a minimum allowance of 1 mm.

A large proportion of failures in process plant and vessels are due to corrosion. It is often the prime cause of deterioration and may occur on any part of a vessel. The severity of the deterioration is strongly influenced by the concentration, temperature, and nature of the corrosive agents in the fluids and the corrosion resistance of the construction materials. Corrosion may be of a general nature with fairly uniform deterioration or may be very localised with severe local attack. Erosion is often localised especially at areas of high velocity or impact. Occasionally corrosion and erosion combine to increase rates of deterioration.

Erosion is a particular problem for solids handling in pipework, ducts and dryers. It occurs primarily at sites where there is a flow restriction or change in direction including valves, elbows, tees and baffles. Erosion is promoted by the presence of solid particles, by drops in vapours, bubbles in liquids or two-phase flow. Conditions that can cause severe erosion include pneumatic conveying, wet steam flow, flashing flow and pump cavitation. If erosion is likely to occur then more resistant materials should be specified or the material surface protected in some way. For example, plastic inserts can be used to protect erosion-corrosion at the inlet to heat exchanger tubes.

Specific Equipment - Mechanical Design

Design issues, codes and standards applicable to several general categories of equipment have been identified and are discussed below in further detail:

- Pressure Vessels;
- Other Vessels (including Storage Tanks);
- Reactor Design;
- Heat Exchange Equipment;
- Furnaces and Boilers;
- Rotating Equipment.

Pressure Vessels

There are numerous texts available on the details of pressure vessel design however the basis of the design of pressure vessels is the use of appropriate formulae for vessel dimensions in conjunction with suitable values of design strength.

Pressure vessels can be divided into `simple vessels' and those that have more complex features. The relevant standards and codes provide comprehensive information about the design and manufacture of vessels and vessel design and fabrication is an area well covered by standards and codes. In general terms outright failure of a properly designed, constructed, operated and maintained pressure vessel is rare.

Design and manufacture are normally carried out to meet the requirements of national and international standards with one of the earliest being the AOTC 1939/48/58 `Rules for the construction, testing and scantlings of metal arc welded steel boilers and other pressure vessels'. Generally, pressure vessel design codes cover equipment such as reactors, distillation columns, storage drums, heaters, reboilers, vaporisers, condensers, heat exchangers, bullets, spheres etc. Basically, any equipment with a "shell" that may experience some internal pressure is covered.

Design Considerations

Factors that should be considered in the design process for pressure vessels include:

- Internal and external static and dynamic pressures;
- Ambient and operational temperatures;
- Weight of vessel and contents;
- Wind loading;
- Residual stress, localised stress, thermal stress etc.;

- Stress concentrations;
- Reaction forces and moments from attachments, piping etc;
- Fatigue;
- Corrosion/erosion;
- Creep;
- Buckling.

Pressure vessels are subject to a variety of loads and other conditions that cause stress and can result in failure and there are a number of design features associated with pressure vessels that need to be carefully considered.

- Discontinuities such as vessel ends, changes of cross-section and changes of thickness;
- Joints (bolted and welded);
- Bimetallic joints;
- Holes and openings;
- Flanges;
- Nozzles and connections;
- Bolt seating and tightening;
- Supports and lugs.

Consideration should also be given to other parts of the vessel not directly within the pressure envelope, but critical to vessel integrity i.e., any failure which could lead to breach of the pressure boundary e.g., vessel skirt or support legs. Other factors which require careful consideration include; a means of in-service periodic examination i.e., a means of determining the internal condition of the vessel by the provision of access openings; a means of draining and venting the vessel; and means by which the vessel can be safely filled and discharged.

Materials of Construction
Vessels

Materials used for the manufacture of pressure vessels should have appropriate properties for all operating conditions that are reasonably foreseeable, and for all test conditions. They should be sufficiently chemically resistant to the fluid contained and not be significantly affected by ageing. The materials should be selected in order to avoid corrosion effects when the various materials are put together. Steel is the most common material of construction, including mild steel, low alloy steel, and stainless steel. It is often operating process temperature that determines the material used, but other equally important factors such as corrosion/erosion allowance, low temperature application etc. can determine selection. Clearly in the choice of material selection, it is important that the material selected not only has properties which are suited to that particular application, but also that its suitability with regard to fabrication is also considered. Several different methods are used to construct pressure vessels, most however are constructed using welded joints. Where a European, American or British code is used for vessel design and specific materials are quoted within the code, it is important that the correct materials are used in order that the design is not invalidated.

Liners

Where carbon steel will not resist expected corrosion or erosion or could cause contamination of the product, vessels may be lined with other metals or non-metals. A lined vessel is usually more economical than one built of solid corrosion resistant material. Metallic liners are installed in various ways. They may be an integral part of the plate material rolled or bonded before fabrication of the vessel, or they may be separate sheets of metal fastened by welding. Metallic liners may be made of ferritic alloy, Monel alloy, nickel, lead or any other metal resistant to the corrosive agent. Non-metallic liners may be used to resist corrosion and erosion or to insulate and reduce the temperature on the walls of a pressure vessel. The most common materials are reinforced concrete, insulating material, carbon brick, rubber, glass and plastic.

Internals

Many pressure vessels have no internals. Others have internals such as baffles, trays, mesh or strip type packing, grids, bed supports, cyclones, pipe coils, spray nozzles, quench lines, agitators etc. Large vessels may have internal bracing and ties and most vacuum vessels have either internal or external stiffening rings. Heat exchangers have internal tube bundles with baffle and support plates. These internals may be made from a wide range of materials but care should be taken that the materials selected for the internals are compatible with the materials chosen for fabrication of the main components.

Failure Modes

Pressure vessels are subject to a variety of loads and other conditions that cause stress and in certain cases may cause serious failure. Any design should take into account the most likely failure modes and causes of deterioration. Deterioration is possible on all vessel surfaces in contact with any range of organic or inorganic compounds, with contaminants, or fresh water, with steam or with the atmosphere. The form of deterioration may be electrochemical, chemical, mechanical or combinations of all.

- Mechanical Failure

  The most common causes of mechanical failure in process plant are:

  - Faulty materials;
  - Faulty fabrication and assembly;
  - Excessive stress;
  - External loading including reaction forces;
  - Overpressure;
  - Overheating;
  - Mechanical and thermal fatigue;
  - Mechanical shock;
  - Brittle failure;
  - Creep;
  - Corrosion failure.

- Corrosion Failure

  The most common corrosion mechanisms are:

  - General corrosion;
  - Crevice corrosion;
  - Corrosion pitting;
  - External corrosion including corrosion beneath lagging;
  - Stress corrosion cracking;
  - Corrosion fatigue.

Reactor Design

Reactors are often the centre of most processes and their design is of utmost importance when considering the safety hazards of a plant. Reactors are most often considered as pressure vessels and the mechanical design should be in accordance with the codes and standards described earlier.

Reactor design should minimise the possibility of a hazardous situation developing and provide the means for dealing with a hazardous situation should it develop. Arrangements for venting, pressure relief and blowdown need to be adequately addressed in the design. For relief systems, consideration should be given to the implications of the release of reactor contents and containment and control systems may be necessary to prevent a hazardous situation from developing as a result of the discharge of a relief system.

The design of the reactor may affect the efficiency of the reaction process and hence the generation of by-products and impurities. The effectiveness of the reaction step will often determine the requirement for, and complexity of, downstream separation processes. In addition, low conversions may result in large recycles being required.

Many different types of reactor system are available and some of the important criteria to consider are given below:

Addition of reactants - the order and rate of addition of the reactants may affect the rate of reaction and the generation of by-products. The generation of unstable by-products or excessive reaction rates may increase the potential for a hazardous situation to develop. The position of addition of reactants may also be important - sub-surface and directly into an intimate mixing zone within the reactor may result in the minimisation of the generation of reaction by-products;

- Mixing - the agitation system selected for the reactor (if appropriate) may directly influence the efficiency of the reaction and hence the generation of by-products. Consideration should also be given to the consequences of agitation failure in the design of the reaction system. Methods for detecting the failure of a mixing/agitation system and/or stopping the flow of reactants into the reactor may be appropriate especially if there is the possibility of two phases forming on agitation failure which may react exothermically/vigorously when agitation is recommenced.
- Heat removal - for exothermic reactions the control of the reaction system and the heat removal systems should be carefully considered. Consideration should be given to the modes of failure of the control and cooling systems to ensure that the hazards of a runaway exothermic reaction are minimised;

- Phase - the reaction may take place in the gas, liquid or sometimes solid phase. The way in which the reactants are brought into contact may influence the efficiency of the reaction and introduce additional hazards into the reaction system;
- Catalysts - a reaction may require a catalyst in order to promote the required reaction. However, the catalyst may present additional hazards and consideration should be given to the selection of the catalyst system in order to minimise the risks associated. If a catalyst is required then additional separation steps to remove the catalyst may subsequently be required.

The safety report should describe how the reactor system has been designed with the principles of safe design in mind and how the selection of the mixing, chemical addition systems and relief systems have been selected in order to minimise the potential for a major accident.

Rotating Equipment

Process machines are particularly important items of equipment in process plants and in relation to pressure systems since they are required to provide the motive force necessary to transfer process fluids (liquids, solids and gases) from one area of operation to another. A machine system is any reciprocating or rotating device that is used to transfer or to produce a change in properties within a process plant. Examples may include items such as pumps, fans, compressors, turbines, centrifuges, agitators etc. This type of equipment is a potential source of loss of containment. In addition, due to the rotating/vibrating nature of such equipment, pressure and flow fluctuations may be caused and these can affect the operation of other systems.

The basic requirements to define the application for pumps, fans and compressors are usually the suction and delivery pressures, the flow rate required and the pressure loss in transmission. Special requirements for certain industrial sectors may also impose restrictions on the materials of construction to be used or the type of device that can be considered. Many designs have become standardised based on experience and numerous standards (API standards, ASME standards, ANSI standards) have become available. These standards often specify design, construction and testing details such as material selection, shop inspection and tests, drawings, clearances, construction procedures etc

The choice of material of construction is dictated by consideration of corrosion, erosion, personnel safety and containment and contamination.

Pumps

Many pumps are of the centrifugal type, although positive displacement types (such as reciprocating and screw types) are also used. Pumps are available throughout a vast range of sizes and capacities and are also available in a wide range of materials including various metals and plastics. Sealing of pumps is a very important consideration and is discussed later. The primary advantage of a centrifugal pump is its simplicity. Pumps are particularly vulnerable to mal-operation and poor installation practices. Proper installation and high-quality maintenance are essential for safe operation.

Problems associated with centrifugal pumps can include bearing and seal failure. Cavitation (the collapse of vapour bubbles in a flowing liquid leading to vibration, noise and erosion) and dead head running (attempting to run a pump without an outlet for the fluid, for example against a closed valve) can also result in damage to the pumping equipment. Misalignment between pump and motor is also a common cause of catastrophic failure.

Seal-less or canned pumps are often used where any leakage is considered unacceptable. In a canned pump the impeller of the pump and the rotor of the motor are mounted on an integral shaft which is encased so that the process fluid can circulate in the space which is normally the air gap of the motor.

Key parameters for pump selection are the liquid to be handled, the total dynamic head, the suction and discharge heads, temperature, viscosity, vapour pressure, specific gravity, liquid corrosion characteristics, the presence of solids which may cause erosion etc.

Compressors

Both positive displacement and centrifugal compressors are used in the process industry. They are complex machines and their reliability is crucial. It is very important that they are maintained to high operational standards. Centrifugal compressors are by far the most common although compression is generally lower than that given by reciprocating machines. They are used in both process gas and refrigeration duties. On centrifugal compressors some of the principal malfunctions include rotor or shaft failure, bearing failure, vibration and surge. Reciprocating compressors are utilised for higher compression requirements. They may be either single or multi-stage units. Air compressors for dry air require special consideration and specific codes and standards exist.

Fans
The main applications for fans are for high flow, low pressure applications such as supplying air for drying, conveying material suspended in a gas stream, removing fumes, or in condensing towers. These units can be either centrifugal or axial flow type. They are simple machines but proper installation and maintenance is required to ensure high reliability and safe operation.

Vibration
One of the main causes of failure of rotating equipment is vibration. This often causes seal damage or fatigue failure and subsequent leakage and can result in a major accident. Numerous factors can result in vibration occurring including cavitation, impeller imbalance, loose bearings and pulses in the pipe. ASME standards recommend that pumps should be periodically monitored to detect vibration that should normally fall within prescribed limits as determined by the manufacturer. This should be initially confirmed on installation and then periodically checked. If measured levels exceed prescribed values, then preventative maintenance is required and should be performed. By collection and analysis of vibration signatures of rotating equipment it is possible to identify which components of the system are responsible for particular frequencies of the vibration signal. It is then possible to identify the component that is deteriorating and responsible for the vibration that is occurring.

Seals
Seals are very important and often critical components in large rotating machinery and in systems which are flanged/jointed such as heat exchangers or pipework systems. Failure of a sealing arrangement can lead to loss of containment and a potential for a major accident. Numerous different types of sealing arrangement exist for rotating equipment. There are many factors that govern the selection of seals for a particular application including the product being handled, the environment which the seal is installed in, the arrangement of the seal, the equipment the seal is to be installed in, secondary packing requirements, seal face combinations, seal gland plate arrangements, and main seal body etc. The materials used for seals should always be compatible with the process fluids being handled.

There are three principal methods of sealing the point at which a rotating shaft enters a pump, compressor, pressure vessel or similar equipment:

- Conventional stuffing box with soft packing;
- Hydrodynamic seal, where rotating vanes keep the shaft free;

- Mechanical seals.

Stuffing boxes and glands with packing are commonly used. Some product leakage is normal both lubricating and cooling the packing material. The chief advantages of this type of sealing arrangement are the simplicity and the ease of adjustment or replacement. The disadvantages are the necessity of frequent attention and the inherent lack of integrity of such a system.

Mechanical seals are the next most commonly employed arrangement. They are used in applications where a leak tight seal of almost any fluid is required. Mechanical seals find their best application where fluids should be contained under substantial pressure. They can range from the simplest single seal arrangement to complicated sophisticated double seals with monitoring of the interspace. Some mechanical seals are assemblies of great complexity and consist of components manufactured to very high tolerances. They are often fitted as complete cartridge type units. Some sealing arrangements require constant lubrication often from the process fluid itself whilst others require external lubrication arrangements.

Maintenance, Inspection and Monitoring

Plant equipment may be monitored during commissioning and throughout its operational life. This monitoring may be carried out on the basis of performance or condition or both. Performance monitoring is not discussed in detail in this Technical Measures Document. However, the predominant techniques and parameters employed are flow, pressure, temperature, power etc. The alternative to performance monitoring is condition monitoring of which there are a number of techniques. The aim of such techniques is to identify deterioration and pre-empt imminent failures and so secure reliable/available plant, particularly for production and safety critical items. Some of these techniques are identified below:

- Vibration monitoring;
- Shock pulse monitoring;
- Acoustic emission monitoring;
- Oil analysis
- Critical machines

All machine systems should be assessed according to the hazard presented if the machine or any associated protective system should fail.

Machine systems that have been assessed to present unacceptable consequences if the machine or protective system should fail may be classified as a `Critical Machine System' and given specific attention during operation including additional maintenance and monitoring.

Assessments should be based on:

- Potential consequences of any loss of containment);
- Potential consequences of the failure of the process;
- Potential damage caused by mechanical failure.

Plant Layout
Plant layout is often a compromise between a number of factors such as:

- The need to keep distances for transfer of materials between plant/storage units to a minimum to reduce costs and risks;
- The geographical limitations of the site;
- Interaction with existing or planned facilities on site such as existing roadways, drainage and utilities routings;
- Interaction with other plants on site;
- The need for plant operability and maintainability;
- The need to locate hazardous materials facilities as far as possible from site boundaries and people living in the local neighbourhood;
- The need to prevent confinement where release of flammable substances may occur;
- The need to provide access for emergency services;
- The need to provide emergency escape routes for on-site personnel;
- The need to provide acceptable working conditions for operators.

The most important factors of plant layout as far as safety aspects are concerned are those to:

- Prevent, limit and/or mitigate escalation of adjacent events (domino);
- Ensure safety within on-site occupied buildings;

- Control access of unauthorised personnel;

- Facilitate access for emergency services.

In determining plant layout designers should consider the factors in outlined in the following sections.

Inherent safety

The major principle in Inherent Safety is to remove the hazard altogether. The best method to achieve this is to reduce the inventory of hazardous substances such that a major hazard is no longer presented. However, this is not often readily achievable and by definition no COMAH facility will have done so. Other possible methods to achieve an Inherently Safer design are:

- Intensification to reduce inventories;
- Substitution of hazardous substances by less hazardous alternatives;
- Attenuation to reduce hazardous process conditions i.e., temperature, pressure;
- Simpler systems/processes to reduce potential loss of containment or possibility of errors causing a hazardous event;
- Fail-safe design e.g., valve position on failure.

Plant layout considerations to achieve Inherent Safety are mainly those concerned with domino effects (see below).

The Dow / Mond Indices

These hazard indices are useful for evaluating processes or projects, ranking them against existing facilities, and assigning incident classifications. They provide a comparative measure of the overall risk of fire and explosion of a process and are useful tools in the plant layout development stage since they enable objective spacing distances to be considered at all stages.

Although these are useful rule-of thumb methodologies for first consideration of plant layout, they do not replace risk assessment. The distances derived between plant units using these systems are based upon engineering judgement and some degree of experience rather than any detailed analysis.

Domino effects

Hazard assessment of site layout is critical to ensure consequences of loss of containment and chances of escalation are minimised. Domino may be by fire, explosion (pressure wave and missiles) or toxic gas cloud causing loss of control of operations in another location.

Fire

A fire can spread in four ways:

- Direct burning (including running liquid fires);
- Convection;
- Radiation;
- Conduction.

The spread of fire from its origin to other parts of the premises can be prevented by vertical and horizontal compartmentation using fire-resisting walls and floors. Consideration should also be given to the spread of flammable material via drains, ducts and ventilation systems. Delayed ignition following a release may result in spread of flames through such systems via dispersed flammable gases and vapours.

Protection against domino effects by convection, conduction and radiation can be achieved by inherent safety principles i.e., ensuring that the distances between plant items are sufficient to prevent overheating of adjacent plants compromising safety of those plants also. Where this is not possible due to other restrictions, other methods such as fire walls, active or passive fire protection may be considered.

Explosion

Explosion propagation may be directly by pressure waves or indirectly by missiles. As for fires, inherently safe methods that should be considered are:

- arranging separation distances such that damage to adjacent plants will not occur even in the worst case;
- provision of barriers e.g., blast walls, location in strong buildings;
- protecting plant against damage e.g., provision of thicker walls on vessels;
- directing explosion relief vents away from vulnerable areas e.g., other plants or buildings, roadways near site boundaries.

Toxic gas releases

Toxic gas releases may cause domino effects by rendering adjacent plants inoperable and injuring operators. Prevention/mitigation of such effects may be affected by provision of automatic control systems using inherently safer principles and a suitable control room.

Reduction of consequences of event on and off Site

In addition to the measures described in the sections above, Plant Layout design techniques applicable to the reduction of the risks from release of flammable or toxic materials include:

- Locating all high-volume storage of flammable / toxic material well outside process areas;
- Locating hazardous plant away from main roadways through the site;
- Fitting remote-actuated isolation valves where high inventories of hazardous materials may be released into vulnerable areas;
- Provision of ditches, dykes, embankments, sloping terrain to contain and control releases and limit the safety and environmental effects;
- Siting of plants within buildings as secondary containment;
- Siting of plants in the open air to ensure rapid dispersion of minor releases of flammable gases and vapours and thus prevent concentrations building up which may lead to flash fires and explosions;
- Hazardous area classification for flammable gases, vapours and dusts to designate areas where ignition sources should be eliminated.

Risk management techniques should be used to identify control measures that can be adopted to reduce the consequences of on or off-site events

Operating Procedures

General Principles for Pilot Plant Operation

There have been numerous recorded incidents where failings by operators have been the major contributing cause of major accidents. Provision of clear, concise and accurate operating procedures is the most effective measure to prevent, control and mitigate such events.

Operating procedures should clearly lay down instructions for operation of process plant that take into consideration COSHH, manual handling, permit to work, PPE Regulations, quality, HAZOP, and SHE requirements. The procedure should represent a definition of good or best practice that should be adhered to at all times. Process operatives should be provided with guidance concerning the required operating philosophy to ensure that they comply with procedural requirements.

Adequate training should be provided to ensure that operators are fully conversant with written procedures.

It is important that operating procedures should always reflect plant practice, and vice versa.

Provision of Comprehensive Written Operating procedures

Comprehensive written operating procedures should be generated where applicable that address:

- Standard operating procedures and operating philosophy;
- Abnormal operating procedures;
- Temporary operating procedures;
- Plant trials;
- Emergency operating procedures;
- Commissioning;
- Plant Start-up;
- Plant Shut-down;
- Bulk loading and unloading;
- Process change;
- Plant change.

These procedures should cover the following:

- Material safety data (all chemical MSDS documentation);

- Plant operatives should have an awareness and understanding of material safety data for raw materials, intermediates, products and effluent / waste;
- Control measures and personal protective equipment;
- Location of plant where process to be undertaken;
- Roles and responsibilities of individuals involved in plant operations;
- Plant fit for purpose;
- The condition of main process plant and equipment (clean, empty etc. as appropriate) should be established as being fit for purpose;
- The condition of ancillary process plant and equipment (clean, empty etc. as appropriate);
- Plant correctly set-up for processing;
- Process monitoring and recording;
- Monitoring and recording of key process parameters (temperature, pressure etc.) in plant logs;
- Quality;
- Sampling of raw materials, intermediates, products and effluent/waste;

Operating procedures should be controlled documents, generally covered under the company's quality system and thus kept fully up to date. Any changes should be fully controlled and documented and should be subject to company change procedures. Standard operating procedures may generally be revised for the following reasons:

- Introduction of new equipment into the process;
- Introduction of new chemicals into the process;
- Significant change to process, task, personnel or equipment covered by the procedure;
- Plant trials have been successful and need to be incorporated into standard operating procedures.

Clear definition of where limits of intervention cease and reliance upon the control systems interface begins is a critical step in defining the operating procedures for a given plant or process. During the hazard and operability stage, the justification of reliance upon human intervention rather than automated systems should be established. This should be assessed in more depth in a subsequent risk assessment.

Commissioning procedures

Commissioning of process plant is the practical test of the adequacy of prior preparations, including training of operating personnel and provision of adequate operating instructions. Since the possibility of unforeseen eventualities cannot be eliminated during this period when operating experience is being gained, the need for safety precautions should be reviewed. This should form part of the HAZOP / Risk Assessment processes applied to the installation. Full written operating instructions should be provided for all commissioning activities.

Commissioning Procedures document a logical progression of steps necessary to verify that installed plant is fully functional and fit for purpose. A general sequence of steps in commissioning may typically include:

- System Configuration Check;
  The purpose of this activity is to trace all pipework and connections to verify the system configuration, and to visually inspect items of equipment to ensure that they are clean, empty and fit for purpose as appropriate prior to undertaking water trials.
- Instrumentation System Check - Verification of Alarms and Trips;
  The purpose of this activity is to ensure that all instrumentation, alarm settings, microprocessor signals and hardwire trips pertaining to the installation are functional. This will also check that signals from any remote instrumentation are displayed locally and are being correctly relayed to any interface rack, as well as to the computer system.
- Flushing and Cleaning of Lines and Vessels with Water;
  The purpose of this activity is to clean all items of pipework and the vessels that make up the installation. This task shall also ensure that there are no obstructions, blockages or any potential contaminants in any of the process lines or vessels that may have resulted from materials being left inside the system from the construction phase. If chemicals incompatible with water are to be used, it is important that the pipelines and equipment are thoroughly dried prior to introduction of the chemicals. This is normally done by passing dry air through the plant.
- Assessment of Ancillary Equipment;
  The main aim of this assessment is to verify the performance of all ancillary equipment. This may include pumps, fans, heat exchangers, condensers etc.
- Calibration of Vessels and Instrumentation;
  The purpose of this activity is to check the calibration and performance of all vessels and instrumentation pertaining to the installation. To a certain extent this will be carried out in conjunction with the system pre-checks to ensure that the correct set points and alarm points have been established for use in the water trials.
- Start Up Protocol;
  The purpose of this procedure is to provide guidance for bringing the installation online starting from an empty non-operational system.

- Shut Down Protocol;

  The purpose of this procedure is to provide guidance for taking the installation offline starting from a fully operational system.
- Chemical Trials;

  The aim of this activity is to verify the performance of the installation by simulating 'live' conditions by following standard procedures.
- Handover

Each section should be read in detail to gain understanding about the particular requirements of the activity prior to undertaking the activity itself and completing the associated check list. The checklist will serve as a permanent record of the activity and can be reviewed if future modifications are undertaken.

It is assumed that prior to the commencement of commissioning activities that full support from plant personnel has been obtained.

Start-up / shutdown procedures

Many potential hazards can be realised during start-up or shut-down of plant or process. Specific operating procedures should be provided which take account of all eventualities. For some specific plant items, start-up is known to present particular additional hazards; some examples of these are:

- Dryers – when starting up a drying system after maintenance or a plant shutdown, the actual temperature the dryer might reach before settling out with the control system may result in an increased chance of a dust explosion;
- Vessels, Tanks, Reactors – ignition of flammable vapours introduced may occur for systems relying on elimination of oxygen to prevent explosions, unless inert gas purging is carried out effectively;
- Reactors – start-up of batch reactors after agitator failure may cause an uncontrollable exothermic reaction.

The start-up and shut-down procedures should be ordered and phased so that interlinked plant operations can resume or cease in a safe and controlled manner.

Emergency procedures

Any potential deviations to normal operation that cannot be addressed by design or control identified in the Hazard and Operability studies should be covered by emergency procedures. These should detail how to make plant and process safe, minimising risks to operators at all stages. They should cover PPE (personal protective equipment), the level of intervention which is safe and when to evacuate. The procedures will need to tie in closely with the on and off-site emergency plans.

Management / supervision

A clear management structure should be in place that defines competent responsible person(s) for generation of operating procedures and supervision of plant and personnel. The role of the supervisor in terms of training of operators, overseeing certain critical operations and checking of logs and other activities to ensure compliance with operating procedures. This should fulfil the requirements of the company's health and safety policy.

Human factors

The appropriate design of a procedure is critical in the reduction of human error within process operations. The benefits of procedures are that they can aid an operator when they are faced with a complex diagnosis, or they can act purely as an aide memoir during non-critical routine operations.

The following section provides human factors guidance on the production and implementation of procedures.

Generally, there are four types of procedure:

- Procedures that provide general operating guidance;
- Procedures that provide an aid to meeting operating aims;
- Procedures that are mandatory and prescribe behaviour; and
- Procedures that are used as a training tool.

Each of the procedure types listed above all conform to the same general human factors principals. These are discussed below.

Task analysis

The content of important procedures should be based on some form of formal task analysis method to ensure that the procedure accurately describes the task it refers to. On some plants a process may have a safety-related action or task that has become an accepted 'unofficial' part of the procedure, but which is not documented anywhere. In this situation the task analysis will pick up on this and allow it to be incorporated into the procedures. Conversely, any dangerous actions that an operator might routinely carry out will also be detected.

The most commonly used method of task analysis is Hierarchical Task Analysis (HTA). Further information on this method and others can be found in 'A Guide to Task Analysis edited by B. Kirwan and L. K. Ainsworth.

Operating instructions should be close to the user and kept up to date. The following issues should be considered in assessing operating procedure documentation:

- There should be no easier, more dangerous alternatives than following the procedure.

- There should be a suitable QA system in place to ensure that the procedures can be kept up to date and that any errors are quickly detected and hence corrected.
- The procedures should not be needlessly prescriptive. The best way of ensuring that procedures do not become overly prescriptive is through involving the operator during the design stage.
- Procedures should contain information on the requirements for the wearing of personal protective equipment during the task.
- Any risks to the operator should be documented at the start of the procedure, based on a risk assessment of the task.
- An appropriate method of coding each procedure should be used.
- Each time a procedure is produced it should be dated and also marked, where appropriate, with a shelf life, i.e. 'This procedure is only valid for six months after the date hereon'.
- There should be no ambiguity between which procedures apply to which situations.
- Procedures do not always have to be paper based.
- At the start of the procedure an overview of the task should be provided.
- Prerequisites should be presented clearly at the start of the procedure to ensure that the operator can check that it is safe to proceed.
- The most important information on the page should be identified and this should be designed to be the most prominent information.
- Separate headings should be used to differentiate clearly between sub tasks.
- Any warnings, cautions or notes should be placed immediately prior to the instruction step to which they refer.
- Language should be kept as simple as possible, i.e., use nomenclature familiar to the operator.
- The nomenclature should be consistent with that on controls or panels.
- Symbols, colours, and shapes used for graphics should conform to industry standards.

Validation
A procedure should always be formally validated prior to it being issued. The best method to achieve this is a comprehensive walk-through assessment of the procedure in the plant, or with reference to the relevant plant drawing when an in-plant assessment is not possible.

Maintenance Procedures
The following aspects should be considered with respect to Maintenance Procedures:

- Human factors;
- Poorly skilled work force;
- Unconscious and conscious incompetence;

- Good maintainability principles;
- Knowledge of failure rate and maintainability; and
- Clear criteria for recognition of faults and marginal performance.

The following issues may contribute towards a major accident or hazard:

- Failure of safety critical equipment due to lack of maintenance;
- Human error during maintenance;
- Static or spark discharge during maintenance in an intrinsically safe zone;
- Incompetence of maintenance staff; and
- Poor communication between maintenance and production staff.

A Safety Report should address the following points:

- Whether the company maintenance regimes (planned, risk-based, reliability centred, condition based or breakdown maintenance) are adequate for each plant item which has a safety function;
- Whether proof check periods quoted for safety critical items are adequate to ensure risks are within acceptable limits;
- Whether the procedures to ensure quoted proof check periods for safety critical items are adhered to;
- Whether the company Safety Management System includes adequate consideration of maintenance of plant, instrumentation and electrical systems;
- Whether maintenance staff have been sufficiently trained to recognise plant or equipment failing during maintenance inspections;
- Whether maintenance staff have been sufficiently informed, instructed, trained and supervised to minimise a potential human failing during maintenance;
- Whether maintenance schedules are managed and regularly inspected and reviewed;
- Whether Human factors (stress, fatigue, shift work, attitude) are addressed;
- Whether sufficient precautions are taken prior to maintenance of hazardous plant and equipment (isolation, draining, flushing, environmental monitoring, risk assessments, permits to work, communication, time allotted for the work);
- Whether the maintenance staff are aware of the type of environment they are working in (flammable, corrosive, explosive, zones 0, 1 & 2);
- Whether the maintenance staff use the correct equipment in the workplace during re-conditioning, replacement and re-commissioning (static free, intrinsically safe, flameproof, PPE/RPE);

- Whether sufficient maintenance systems are in place during productive assistance, servicing, running of plant, plant shutdown and plant breakdown;
- Whether procedures are in place to provide detailed operating instructions for re-commission plant after maintenance, which have been subjected to risk assessments;
- Whether sufficient reporting systems are in place so that corrective maintenance can be applied to mitigate a major accident or hazard.

Major Hazards

Major hazards could arise from the following:

- The lack of control of spares such that incorrect materials or items outside specification (e.g., non-flameproof equipment) are used in replacement of plant items leading to increased risk of loss of containment, fire or explosion;
- Failure to drain and/or isolate plant prior to dismantling causing release of flammable or toxic substances;
- Maintenance being performed incompetently (particularly alarm/action set points on instruments incorrectly set, alignment of couplings on pumps and agitators causing overheating, motors running in wrong direction, safety features left disconnected/dismantled, gaskets left out, bolts torqued incorrectly or bolts missing, non-return valves orientation incorrect, pipework/flexibles incorrectly connected/installed, pipeline spades/orifice plates left in/removed, relief valve springs overtightened, bursting discs orientation incorrect/left out);
- Scheduled maintenance not being undertaken as required or breakdown maintenance inadequate, leading to unrevealed failures of safety critical items;
- Lack of knowledge by maintenance staff of the working environment where maintenance is being carried out (i.e., lack of risk assessments, warning signs, method statements, emergency procedures), leading to ignition of flammable substances (e.g., heat sources such as cigarettes or welding, static and electrical discharge, use of non-spark-resistant tools) or injury/fatality from incorrect personal protective equipment (e.g., respirators) being worn;
- Unauthorised staff performing maintenance functions; and
- Failure to re-commission plant correctly after maintenance to ensure that operations are not adversely affected in terms of safety considerations (e.g., contamination, flow rate changes, heat transfer rate changes, mass transfer rate changes).

Control Systems

Whilst the proposed pilot plants will almost certainly be subject in their entirety to manual operation, it may be appropriate that instrumental control and a level of automation will be introduced.

An instrumented control system is an electrical, electronic, or programmable electronic system (E/E/PES) which may perform some or all of the following functions:

- Monitoring, recording and logging of plant status and process parameters;
- Provision of operator information regarding the plant status and process parameters;
- Provision of operator controls to affect changes to the plant status;
- Automatic process control and batch/sequence control during start-up, normal operation, shutdown, and disturbance. i.e., control within normal operating limits;
- Detection of onset of hazard and automatic hazard termination (i.e., control within safe operating limits), or mitigation;
- Prevention of automatic or manual control actions which might initiate a hazard.

These functions are normally provided by, alarm, protection (trip, interlocks and emergency shutdown), and process control systems.

These engineered systems are individually and collectively described as control systems, and may be independent, or share elements such as the human interface, plant interface, logic, utilities, environment and management systems.

The human interface may comprise a number of input and output components, such as controls, keyboard, mouse, indicators, annunciators, graphic terminals, mimics, audible alarms, and charts.

The plant interface comprises inputs (sensors), outputs (actuators), and communications (wiring, fibre optic, analogue/digital signals, pneumatics, fieldbus, signal conditioning, barriers, and trip amplifiers).

The logic elements may be distributed, and linked by communications, or marshalled together and may be in the form of relays, discrete controllers or logic (electronic, programmable or pneumatic), distributed control systems (DCS), supervisory control and data acquisition (SCADA), computers (including PCs), or programmable logic controllers (PLC). The logic elements may perform continuous control functions, or batch or change of state (e.g., start-up/shut-down) sequences. It should also be noted that logic functions may be distributed to be undertaken within smart sensors or actuators.

Utilities are the power supplies and physical elements required for the systems, such as electricity and instrument air.

Environment is the physical accommodation and surroundings in which the control systems (including the operator) are required to work, including physical accommodation or routings, environmental conditions (humidity, temperature, flammable atmospheres), and external influences such as electromagnetic radiation and hazards which might affect the operation of the control system during normal or abnormal conditions such as fire, explosion, chemical attack etc.

Modern instrumented control systems are generally electrical, electronic or programmable electronic systems (E/E/PES), but some purely pneumatic systems may still be in operation.

Safety related systems
A control system or device is deemed to be safety related if it provides functions which significantly reduce the risk of a hazard, and in combination with other risk reduction measures, reduces the overall risk to a tolerable level, or if it is required to function to maintain or achieve a safe state for the equipment under control (EUC).

These functions are known as the safety functions of the system or device and are the ability to prevent initiation of a hazard or detect the onset of a hazard, and to take the necessary actions to terminate the hazardous event, achieve a safe state, or mitigate the consequences of a hazard.

All elements of the system which are required to perform the safety function, including utilities, are safety related, and should be considered part of the safety related system.

Safety related control systems may operate in low demand mode, where they are required to carry out their safety function occasionally (not more than once/year) or in high demand (more than once/year) or continuous mode where failure to perform the required safety function will result in an unsafe state or place a demand on another protective system. The likelihood of failure of a low demand system is expressed as probability of failure on demand, and as failure rate per hour for high/continuous demand systems.

Safety related control systems operating in continuous or high demand mode where the E/E/PES is the primary risk reduction measure have been known as HIPS (high integrity protective systems). However, use of such systems does not circumvent the need for a hierarchical approach to risk reduction measures such as inherent safety, and careful consideration of prevention of common mode failures by use of diverse technology and functionality (such as relief valves), independent utilities and maintenance and test procedures, physical separation, and external risk reduction (such as bunds). Measures should favour simple technological solutions rather than complex ones. The lowest failure rate which can be claimed for high integrity systems operating in continuous or high demand mode is 10^{-9} dangerous failures per hour.
It should be noted that control systems for equipment under control which are not safety related as defined above may also contribute to safety and should be properly designed, operated and maintained. Where their failure can raise the demand rate on the safety related system, and hence increase the overall probability of failure of the safety related

system to perform its safety function, then the failure rates and failure modes of the non-safety systems should have been considered in the design, and they should be independent and separate from the safety related system.

Safety related systems

A control system or device is deemed to be safety related if it provides functions which significantly reduce the risk of a hazard, and in combination with other risk reduction measures, reduces the overall risk to a tolerable level, or if it is required to function to maintain or achieve a safe state for the equipment under control (EUC).

These functions are known as the safety functions of the system or device and are the ability to prevent initiation of a hazard or detect the onset of a hazard, and to take the necessary actions to terminate the hazardous event, achieve a safe state, or mitigate the consequences of a hazard.

All elements of the system which are required to perform the safety function, including utilities, are safety related, and should be considered part of the safety related system.

Safety related control systems may operate in low demand mode, where they are required to carry out their safety function occasionally (not more than once/year) or in high demand (more than once/year) or continuous mode where failure to perform the required safety function will result in an unsafe state or place a demand on another protective system. The likelihood of failure of a low demand system is expressed as probability of failure on demand, and as failure rate per hour for high/continuous demand systems.

Safety related control systems operating in continuous or high demand mode where the E/E/PES is the primary risk reduction measure have been known as HIPS (high integrity protective systems). However, use of such systems does not circumvent the need for a hierarchical approach to risk reduction measures such as inherent safety, and careful consideration of prevention of common mode failures by use of diverse technology and functionality (such as relief valves), independent utilities and maintenance and test procedures, physical separation, and external risk reduction (such as bunds). Measures should favour simple technological solutions rather than complex ones. The lowest failure rate which can be claimed for high integrity systems operating in continuous or high demand mode is 10^{-9} dangerous failures per hour.

It should be noted that control systems for equipment under control which are not safety related as defined above may also contribute to safety and should be properly designed, operated and maintained. Where their failure can raise the demand rate on the safety related system, and hence increase the overall probability of failure of the safety related system to perform its safety function, then the failure rates and failure modes of the non-safety systems should have been considered in the design, and they should be independent and separate from the safety related system.

System integrity

The integrity required of a safety related system depends upon the level of risk reduction claimed for the safety function to be performed.

Safety integrity is the probability that safety related system will satisfactorily perform the required safety function under all stated conditions within a stated period of time when required to do so.

Safety integrity is therefore a function of performance and availability.

Performance is the ability of the system or device to perform the required safety function in a timely manner under all relevant conditions so as to achieve the required state.

Availability is the measure of readiness of the system to perform the required safety function on demand and is usually expressed in terms of probability of failure on demand.

Performance and availability depend on:

- Proper design or selection, installation and maintenance and testing of the plant interfaces, including sensors actuators and logic, for the required duty and full range of process and environmental conditions under which they will be required to operate, including, where necessary, any excursions beyond the safe operating limits of the plant;
- Accuracy and repeatability of the instrumentation;
- Speed of response of the system;
- Adequate margins between normal and safe operating limits and the system settings;
- Reliability;
- Survivability from the effects of the hazardous event or other external influences such as power system failure or characteristics, lightning, electromagnetic radiation (EMR), flammable, corrosive or humid atmospheres, temperature, rodent attack, vibration physical impact, and other plant hazards;
- Independence (the ability of the system to act alone, without dependence on other protective measures, control systems or common utilities or to be influenced by them.

The following measures are required to ensure adequate performance and availability of the safety related system:

- Protection against random failures by hardware reliability, fault tolerance (e.g., by redundancy) and fault detection (diagnostic coverage, and proof testing);

- Protection against systematic and common mode failures by a properly managed safety lifecycle, independence from common utilities, common management systems and other protective systems, and by diversity. The lifecycle includes hazard and risk evaluation, specification, design, validation, installation, commissioning, operation, maintenance, and modification.

Integrity levels

Integrity levels for safety related systems may be determined from the hazard and risk analysis of the equipment under control. A number of different methodologies are available, but the process includes identification of hazards and the mechanisms which can initiate them, risk estimation (likelihood of occurrence), and risk evaluation (overall risk based on likelihood and consequences). The risk estimation provides a measure of the risk reduction required to reduce the risk to a tolerable level.

Hazard identification results in the identification of safety functions which are required to control the risk.

The safety functions may then be allocated to a number of different systems including E/E/PES, other technology and external measures.

For each system providing a safety function, a failure rate measure can be assigned which in turn determines the integrity required of the system. alternatively, a qualitative approach (based on the likelihood and consequence of the hazard, and the frequency and level of exposure and avoidability) may be used to define the required integrity.

Alarm systems

Alarm systems alert operators to plant conditions, such as deviation from normal operating limits and to abnormal events, which require timely action or assessment.

Alarm systems are not normally safety related but do have a role in enabling operators to reduce the demand on the safety related systems, thus improving overall plant safety.

The following guidance is considered appropriate in regard to safety related alarm systems:

- The alarm system should be designed in accordance with the designated reliability;
- The alarm system should be independent from the process control system and other alarms unless it has also been designated safety related;
- The operator should have a clear written alarm response procedure for each alarm which his simple, obvious and invariant, and in which he is trained;

- The alarms should be presented in an obvious manner, distinguishable from other alarms, have the highest priority, and remain on view at all times when it is active;
- The claimed operator workload and performance should be stated and verified.

Alarms which are not designated as safety should be carefully designed to ensure that they fulfil their role in reducing demands on safety related systems.

For all alarms, regardless of their safety designation, attention is required to ensure that under abnormal condition such as severe disturbance, onset of hazard, or emergency situations, the alarm system is remains effective given the limitations of human response. The extent to which the alarm system survives common cause failures, such as a power loss, should also be adequately defined.

Alarm settings
The type of alarm and its setting should be established so as to enable the operator to make the necessary assessment and take the required timely action. Settings should be documented and controlled in accordance with the alarm system management controls.

Human interface (alarm presentation)
The human interface should be suitable. Alarms may be presented either on annunciator panel, individual indicators, VDU screen, or programmable display device.

Alarms lists should be carefully designed to ensure that high priority alarms are readily identified, that low priority alarms are not overlooked, and that the list remains readable even during times of high alarm activity or with repeat alarms.

Alarms should be prioritised in terms of which alarms require the most urgent operator attention.

Alarms should be presented within the operator's field of view, and use consistent presentation style (colour, flash rate, naming convention).

Each alarm should provide sufficient operator information for the alarm condition, plant affected, action required, alarm priority, time of alarm and alarm status to be readily identified.

The visual display device may be augmented by audible warnings which should at a level considerably higher than the ambient noise at the signal frequency. Where there are multiple audible warnings, they should be designed so that they are readily distinguished from each other and from emergency alarm systems. They should be designed to avoid distraction of the operator in high operator workload situations. Where both constant frequency and variable frequency (including pulsed or intermittent) signals are used, then the later should denote a higher level of danger or a more urgent need for intervention.

Alarm processing

The alarms should be processed in such a manner as to avoid operator overload at all times (alarm floods). The alarm processing should ensure that fleeting or repeating alarms do not result in operator overload even under the most severe conditions. A number of alarm processing techniques include filtering, deadband, debounce timers, and shelving.

The presentation of alarms should not exceed that which the operator is capable of acting upon, or alternatively the alarms should be prioritised and presented in such a way that the operator may deal with the most important alarms without distraction of the others. Applicable alarm processing techniques include grouping and first-up alarms, eclipsing of lower grade alarms (e.g. suppression high alarm when the high-high activates) suppression of out of service plant alarms, suppression of selected alarms during certain operating modes, automatic alarm load shedding and shelving.

Care should be taken in the use of shelving or suppression to ensure that controls exist to ensure that alarms are returned to an active state when they are relevant to plant operation.

Alarm system management procedures

Management systems should be in place to ensure that the alarm system is operated, maintained and modified in a controlled manner. Alarm response procedures should be available, and alarm parameters should be documented.

The performance of the alarms system should be assessed and monitored to ensure that it is effective during normal and abnormal plant conditions. The monitoring should include evaluation of the alarm presentation rate, operator acceptance and response times, operator workload, standing alarm count and duration, repeat or nuisance alarms, and operator views of operability of the system. Monitoring may be achieved by regular and systematic auditing.

Matters which are not worthy of operator attention should not be alarmed.

Logging may be a suitable alternative for engineering or discrepancy events to prevent unnecessary standing alarms. A system for assessing the significance of such logged events to ensure timely intervention by maintenance personnel may be required.

Protection systems (Trips and Interlocks)

Protective tripping systems provide a defence against excursions beyond the safe operating limits by detecting any excursions beyond set points related to the safe operating limits (i.e. the onset of a hazard) and taking timely action to maintain or restore the equipment under control to a safe state. Trips should not be self-resetting unless adequate justification has been made. Protective interlocks prevent those control actions which might initiate a hazard from being undertaken by an operator or process control system and are by nature self-resetting.

Protection systems should indicate that a demand to perform a safety function has been made and that the necessary actions have been performed.

Independence
Protective systems should be sufficiently independent of the control system or other protective systems (electrical/electronic or programmable). Where there is an interface between systems (e.g. for indication, monitoring or shared components) or shared utilities (e.g. power), environment (e.g. accommodation, wiring routes) or management systems (maintenance procedures, personnel), then the method of achieving independence should be defined, and common cause failures adequately considered.

Measures to defend against common mode failures due to environmental interactions may include physical separation or segregation of system elements (sensors, wiring, logic, actuators or utilities) of different protective systems.

Independence will also be required for protection against systematic and common mode faults. Measures may include use of diverse technology for different protective systems. Where more than one E/E/PES protective system is used to provide the required risk reduction for a safety function, then adequate independence should be achieved by diverse technology, construction, manufacturer or software as necessary to achieve the requires safety integrity level.

Dependence on utilities
The action required from the protective system depend upon the nature of the process. The actions may be passive in nature, such as simple isolation of plant or removal of power, or they may be active in that continued or positive action is required to maintain or restore a safe state, for example by injection of inhibitor into the process, or provision of emergency cooling.

Active protective measures have a high dependence upon utilities and may be particularly vulnerable to common mode failures. The scope of the protective system therefore includes all utilities upon which it depends, and they should have an integrity consistent and contributory to that of the remainder of the system.

Measures taken to defend against common mode failure of utilities will be commensurate with the level of safety integrity required but may include standby or uninterruptable/reservoir supplies for electricity, air, cooling water, or other utilities essential for performance of the safety function. Such measures should themselves be of sufficient integrity.

Survivability and external influences
The protective system should be adequately protected against environmental influences, the effects of the hazard against which it is protecting, and other hazards which may be present. Environmental influences include power system failure or characteristics, lightning, electromagnetic radiation (EMR), flammable atmospheres, corrosive or humid atmospheres, ingress of water or dust, temperature, rodent attack, chemical attack, vibration physical impact, and other plant hazards.
Degradation of protection against environmental influences during maintenance and testing should have been considered and appropriate measures taken. e.g. Use of radios by maintenance personnel may be prohibited during testing of a protective system with the cabinet door open where the cabinet provides protection against EMR.

Protection against random hardware faults
The architecture of the protective system should be designed to protect against random hardware failure. It should be demonstrated that the required reliability has been achieved commensurate with the require integrity level. Defensive measures may include high reliability elements, automatic diagnostic features to reveal faults, and redundancy of elements.

Protection common mode failures
Diversity of elements is not effective for protection against random hardware faults but is useful in defence against common mode failures within a protective system.

Protection systematic failures
Protection against systematic hardware and software failures may be achieved by appropriate safety lifecycles.

Sensing
Sensors include their connection to the process, both of which should be adequately reliable. A measure of their reliability is used in confirming the integrity level of the protective system. This measure should take into account the proportion of failures of the sensor and its process connection which are failures to danger.

Dangerous failures can be minimised by a number of measures such as:

- Use of measurement which is as direct as possible, (e.g. pneumercators provide an inferred level measurement but actually measure back pressure against a head and are sensitive to changes in density due to temperature variations within the process, and to balance gas flow, upon which they are dependant);
- Control of isolation or bleed valves to prevent uncoupling from the process between proof tests or monitoring such that their operation causes a trip;

- Use of good engineering practice and well proven techniques for process connections and sample lines to prevent blockage, hydraulic locking, sensing delays etc.;
- Use of analogue devices (transmitters) rather than digital (switches);
- Use of positively actuated switches operating in a positive mode together with idle current (de-energise to trip);
- Appropriate measures to protect against the effects of the process on the process connection or sensor, such as vibration, corrosion, and erosion;
- Monitoring of protective system process variable measurement (PV) and comparison against the equivalent control system PV either by the operator or the control system.

Proof testing procedures should clearly set out how sensors are reinstated and how such reinstatement is verified after proof testing.

Maintenance procedures should define how sensors/transmitters are calibrated with traceability back to national reference standards by use of calibrated test equipment.

Other matters which will need to have been considered are:

- Cross sensitivities of analysers to other fluids which might be present in the process;
- Reliability of sampling systems;
- Protection against systematic failures on programmable sensors/analysers. The measures taken will depend on the level of variability and track record of the software. 'Smart' transmitters with limited variability software which are extensively proven in use may require no additional measures other than those related to control of operation, maintenance, and modification, whereas bespoke software for an on-line analyser may require a defence in depth against systematic failures;
- Signal conditioning (e.g. filtering) and which may affect the sensor response times;
- Degradation of measurement signals (distance between sensor and transmitter may be important);
- Accuracy, repeatability, hysteresis and common mode effects (e.g. effects of gauge pressure or temperature on differential pressure measurement);
- Integrity of process connections and sensors for containment (sample or impulse lines, instrument pockets are often a weak link in process containment measures).

Actuators and signal conversion
Actuators are the final control elements or systems and include contactors and the electrical apparatus under control, valves (control and isolation), including pilot valves, valve actuators and positioners, power supplies and utilities which

are required for the actuator to perform its safety function, all of which should be adequately reliable. A measure of their reliability is used in confirming the integrity level of the protective system. This measure should consider the proportion of failures of the actuator under the relevant process conditions which are failures to danger.

Actuators are frequently the most unreliable part of the tripping process.

Dangerous failures can be minimised by a number of measures such as:

- Use of 'fail-safe' principles so that the actuator takes up the tripped state on loss of signal or power (electricity, air etc.). e.g. held open, spring return actuator;
- Provision of uninterruptable or reservoir supplies of sufficient capacity for essential power;
- Failure detection and performance monitoring (end of travel switches, time to operate, brake performance, shaft speed, torque etc.) during operation;
- Actuator exercising or partial stroke shutoff simulation during normal operation to reveal failures or degradation in performance. Note this is not proof testing but may reduce probability of failure by improved diagnostic coverage;
- Overrating of equipment.

Other matters which should have been considered are:

- Valves should be properly selected for their duty, and it should not be assumed that a control valve can satisfactorily perform isolation functions;
- Actuators may also include programmable control elements (e.g. SMART instruments) particularly within positioners and variable speed drives and motor control centres. Modern motor control centres may use programmable digital addressing. This introduces a significant risk of introduction of systematic failure and failure modes which cannot be readily predicted. Such an arrangement should be treated with caution. It is normally reasonably practicable for trip signal to act directly upon the final contactor;
- Potential for failure due to hydraulic locking between valves (e.g. trace heated lines between redundant shutoff valves).

Logic systems
Commonly, the logic systems for protective systems are electronic, but programmable and other technology systems (magnetic or fluidic/pneumatic) have been used.

The architecture of the logic system will be determined by the hardware fault tolerance requirements, for example dual redundant channels. Where a high level of integrity for the system is required (SIL3 or SIL4) then diverse hardware between channels may be employed. This should not be confused with diversity of independent protective systems.

Logic systems are likely to incorporate provisions for fault alarms and overrides, for which there should be suitable management control arrangements. They may also provide monitoring of input and output signal lines for detection of wiring (open circuit, short circuit) and sensors/actuators (stuck-at, out of range). Such monitoring may initiate an alarm, a trip action or, in a voting arrangement, disable the faulty element.

Wiring and communications (signal transmission)
Transmitters, communications devices and wiring systems should be arranged to meet the requirements for survivability, protection against external influences and independence.

Independent systems or redundant channels should not share multicore cables with each other or power circuits, and may require diverse routes depending upon the safety integrity level to be achieved.

Measures to protect against failures include:

- Use of fail-safe principles such as DC model (e.g. 4-20 ma loop) for analogue signal transmission diagnosis and alarm of out of range, abnormal, or fault states (such as stuck-at) with defined control system responses for both the sensor and transmitter;
- Cable selection (screening etc.);
- Protection of cables against fire, chemical attack, physical damage etc.;
- Physical separation or segregation of cables and cable routes;
- Routing in benign environments;
- Use of optical fibres to protect against electrical interference;
- Careful attention to lightning protection of data links between buildings.

Use of fieldbus or other digital communication protocols in protective systems should be considered a novel approach requiring a thorough evaluation and demonstration of the safety integrity.

Utilities
Utilities which are required for the protective system to perform its safety function may include power supplies such as electricity, air, inhibitor materials and their propellants, inert gas such as nitrogen, cooling water, steam, pilot flames and their gases all of which should be adequately reliable. Measures such as redundancy, and uninterruptable/reservoir

supplies, and availability monitoring (e.g. loss of air alarm) may be required. Confirmation that the designed capacity of reserves is adequate should be demonstrated by test.

Utilities may also introduce external influences into the protective systems (e.g. from electrical supplies).

Measures to protect against external influences may include:

- Under/Over voltage protection;
- Overcurrent and short circuit protection;
- Use of an uninterruptable power supply or voltage conditioning or filtering;
- Careful attention to lightning protection.

Proof testing

The probability of failure on demand, or the failure rate of a protective system is critically dependent upon the frequency of proof testing and its ability to detect previously unrevealed failures of the system. The proof test interval should therefore be established accordingly, and as a rule of thumb for low demand systems, should be an order of magnitude less than the mean time between failure of the system and the demand rate.

Proof test procedures should be available which specify the success/failure criteria and detail how the test will be performed safely, including any management arrangements, operating restrictions and competence of personnel.

The tests should be arranged to reveal all dangerous failures which have been unrevealed in normal operation including the following measures:

- Tests performed at the conditions which would be expected at trip. (Where test under trip conditions cannot be performed, for example for safety reasons, then measures to ensure that potential failures at trip conditions will be revealed should be clarified);
- End to end tests at appropriate intervals, including proving sample/impulse lines. (Different elements of the protective system may require proof testing at different intervals).

Operation

Procedures should be available which detail the operation of the protective system including:

- Override management (authorisation, security, recording, monitoring and review of overrides, reset requirements);
- Operating instruction for trips;

- Instructions for response to equipment faults including fault alarms. (There should be procedural arrangements in place to ensure timely repair so that mean time to repair criteria can be met).

Maintenance
Procedures should be available for maintenance activities including:

- Maintenance instructions;
- Control of spares (segregation of faulty or non-conforming parts, identification to prevent interchange of similar parts etc.);
- Competence of maintenance personnel;
- Operating restriction during maintenance;
- Control of software back-ups and memory media (E/EPROMS, floppy disks, files on hard disks on portable PCs etc.);
- Post maintenance reinstatement and proof testing.

For systems where a high diagnostic coverage is claimed, for example high integrity high systems, the probability of failure (expressed as failure rate) is critically dependent upon the mean time to repair the faults revealed. For such systems, the repair performance should be monitored and reviewed against the design criteria.

Modification
A management system for control of modifications should be available to ensure that:

- Unauthorised modifications are prevented;
- Authorised modifications are not ill conceived;
- Safety verification to confirm that the required safety function and integrity have been maintained;
- Designed and implementation is carried out by competent persons.

Remote diagnostic systems
Remote diagnostic systems have the potential to cause danger by initiating unexpected operations or by affecting safety functions by software/parameter modification or by diverting the control system processor from time critical functions.

The need for remote diagnosis should be justified, a risk assessment completed, and measures taken to ensure that safety is not affected by normal operation or malfunction of the diagnostic system, including the remote diagnostic terminal and software, communication link, and the control system diagnostic interface and software.

Consideration should be given to:

- Security and control of access;
- Communication between diagnostician and plant personnel;
- Restricted mode of operation; passive (monitoring only), active (control/operator functions), interactive (software changes possible);
- Potential for operation outside restricted mode under fault conditions;
- Protection of safety functions from unauthorised modification;
- Change control;
- Competence of personnel.

Process control systems

Process control systems are primarily implemented for economic reasons. However, those which are not considered safety related should still be designed, installed, operated and maintained so that their failure does not place a rate demand in the protective system which was not anticipated in its design. The dangerous failure modes of the control system should be determined and considered in overall safety system specification. The control system should also be sufficiently independent of the safety systems.

The control system may provide steady state or change of state (start-up, shutdown, batch) control functions. The latter may be implemented by automatic sequences or procedurally under manual control. Control systems should be implemented to provide stable control of the process under all expected normal and upset circumstances, including start-up and shutdown.

The system should be designed to prevent or verify operator commands which might place a demand upon the protective system.

Consideration should be given to failure behaviour so as to minimise the demands placed on the protective systems such as under the following circumstances:

- I/O power failure;
- Main power failure;
- I/O faults (open/short circuit, out of range);
- Module/processor failure (I/O, controller, cell, supervisory);
- Communications failure (at all levels of the architecture).

Consideration should also be given to change control and software back-up systems. As the control system provides control, monitoring and logging functions which significantly aid the operator, consideration should be given to survival of the control system during hazardous events and emergency response.

It should be noted that redundant (non-diverse), cross monitored control processors are extremely vulnerable to common mode failure.

It should be demonstrated that the process control system does not exercise safety functions during sequences and changes of state under its control. For example, where the control system batch sequence controls the mixing of quantities of materials or reagents which, if incorrect quantities are admitted, may result in an unintended reaction, then measures of sufficient safety integrity, other than the control system, should be taken to ensure that the residual risk is as low as reasonably practicable.

Exothermic reactions

Exothermic reactions are particularly demanding in terms of control and protection as they tend to be unstable with aggressive reaction kinetics, and may require risk reduction measures which are required continuously throughout the reaction stage and which rely on utilities such as cooling systems, agitation, inhibitor injection etc.

Thus, loss of any single utility may be a dangerous failure and initiate a hazard (e.g. loss of agitator blades, and hence reduced cooling because of poorer heat transfer, giving rise to a runaway reaction).

The components of the utilities should be considered safety related and provide adequate protection against failure including common mode failures (e.g. loss of electricity) and systematic failures (e.g. failure to fill inhibitor stock vessel). Sufficient diagnostics should be provided to reveal such failures so that timely automatic or manual response can be initiated.

Diagnostics should be designed to reveal the failure as directly as possible, for example:

- Agitator torque rather than shaft speed (which will not reveal blade loss);
- Cooling water flow rather than pump stopped.

Their capacity and capability to deal with the most extreme reaction kinetics (e.g. worst-case mixtures) and limiting conditions (e.g. maximum temperature/pressure achievable under worst case) should also be demonstrated.

Training

General principles

The following aspects should be considered with respect to Training:

- Human factors;
- Poorly skilled work force;
- Poor communication skills; and
- Unconscious and conscious incompetence.

The following issues may contribute towards a major accident or hazard:

- Insufficient training schemes in place to address necessary staff training;
- Operation of plant carried out incorrectly;
- Maintenance of plant carried out incorrectly;
- Unauthorised maintenance carried out by unauthorised persons;
- Unable to recognise hazardous situations;
- Not understanding and fulfilling the requirements of a work permit system;
- Not understanding how to use the technologies in place that control hazardous operations;
- Incompetent staff designing and operating hazardous processes; and
- Not knowing the safety procedures to following in the event of a major accident and hazard (sounding alarms, communication routes, emergency evacuation procedures, fire assembly points).

Contributory factors to consider concerning all aspects of training
Any Safety Report should address the following points:

- The Organisation's perception of training (Investment or cost?);
- The Organisation's ability to analyse training needs and training priorities;
- The Organisation's training strategies, plans, policies, objectives and schemes;
- Resources available for training;
- Whether training details of all employees are kept on file and reviewed;
- Are the trainers sufficiently competent enough to deliver the training requirements;
- Whether training is on-going; and
- Types of success and performance indicators.

Specific training details
The following groups below are likely to require specific types of training courses, which are summarised below under each group sub-heading.

- Decision Makers and Managers;
- Responsible persons (including professional design/process engineers);
- Safety professionals;
- Process operational staff (including engineers);
- Contractors;
- Maintenance staff; and
- Quality control staff.

Specific training details that are required by decision-makers and managers include:

- Academic qualifications and relevant experience;
- Managing safety health and environmental management systems;
- Managerial responsibility for safety and loss prevention;
- Hazard identification (fire/explosive, chemical and physical);
- Reporting accidents;
- Fire prevention and protection;
- Relevant technical training courses to recognise hazardous substances and equipment;
- Information technology;
- Emergency procedures and planning arrangements;
- Training of personnel; and
- Good housekeeping.

Specific training details that are required by responsible persons include:

- Academic qualifications and relevant experience;
- Hazard identification (fire/explosive, chemical and physical);
- Safe systems of work (permits to work, maintenance systems, safe operating procedures, safe use of work equipment, safe handling of hazardous/flammable substances);
- Commissioning, de-commissioning, re-commissioning (after maintenance), shut-down and start-up procedures;
- Emergency quenching and isolation procedures of processes/plant;
- Fire prevention and protection;
- Relevant technical training courses to recognise hazardous substances and equipment;
- Information technology;

- Emergency procedures and planning arrangements;

Specific training details that are required by safety professionals include:

- Academic qualifications and relevant experience;
- Hazard identification (fire/explosive, chemical and physical);
- Relevant technical training courses to recognise hazardous substances and equipment;
- Control of contractors;
- Emergency procedures and planning arrangements;
- Managing safety health and environmental management systems;
- Information technology;

Specific training details that are required by process operational staff, contractors, maintenance staff and quality control staff include:

- Academic qualifications and relevant experience;
- Training specific to plant (operating procedures/maintenance procedures/analytical methods for quality control);
- Firefighting; equipment use and location;
- Information technology;
- Hazard identification (fire/explosive, chemical and physical);
- First aid measures; equipment use and location;
- Rescue methods; equipment use and location;
- Accident reporting systems;
- Correct use of PPE and RPE;
- Safe systems of work (permits to work, maintenance systems, safe operating procedures, safe use of work equipment, safe handling of hazardous/flammable substances);
- Emergency quenching and shutdown procedures of processes/plant;
- Lifting and manual handling techniques;
- Emergency arrangements (alarm raising, recognising warning signs, escape routes and assembly points, spillage procedures, toxic/flammable gas release procedures); and
- Good housekeeping.

Major hazards
Major hazards could arise from the following:

- Incompetently managed safety management systems;
- Unauthorised employees carrying out hazardous tasks;
- Hazardous processes performed by incompetent process operators;
- Maintenance being performed incompetently; and
- Non-compliance with quality and safety procedures.

Storage and Handling of Toxic and Flammable Chemicals

A variety of toxic and flammable chemicals are frequently stored and transported in drums and cylinders. Although individual containers hold relatively small inventories, a single cylinder of a compressed or liquefied toxic gas can present a significant hazard to personnel. Additionally, large quantities of drums and cylinders are often stored together giving rise to potentially large inventories of hazardous materials. The movement and connection / disconnection of drums and cylinders to process plant requires the direct involvement of operating personnel giving rise to the potential for human error to cause incidents.

Storage location

Both the hazards of the material and the size of the inventory need to be considered in determining where a store should be located. Considerations should include the distance from other stored materials, process plant, traffic routes and occupied buildings. Where separation distances are inadequate measures such as firewalls can be employed to reduce the impact of incidents). The operator should demonstrate that the storage location and design has considered site-specific security requirements and the potential for vandalism.

Ventilation

The preferred location for the storage of drummed flammable liquids and compressed / liquefied gases is in the open air, to allow vapours to be dispersed effectively. When located in buildings, the operator should demonstrate that there is an adequate level of ventilation achieved by either the presence of a sufficient size and number of permanent openings such as louvres or mechanical ventilation. If stored indoors, flammable gases such as LPG may only be stored in purpose-built compartments or buildings constructed with fire resistant walls and explosion relief.

Compatibility with other stored materials

Toxic, flammable or self-reactive materials should not in general be stored in the same location. The operator's risk assessment should demonstrate the compatibility of the substances stored and the suitability of the arrangements.

Layout

Drums and cylinders should be stored in a safe manner. Both the height and method of stacking should consider the hazard of the material stored and the construction of the container. Racking or freestanding multi-layer stacks can be used for drummed materials storing low hazard liquids. Consideration should be given to the detection of leaks from containers and the method for collection and disposal of such spills to reduce the possibility of cross-contamination and domino effects. Training should be provided to operators on dealing with spills and emergency procedures. Adequate access for forklift trucks should be provided. Pressurised cylinders and drums should be stored with their valves uppermost in a secure manner. The size of any particular stack should be limited and separation distances should be provided between stacks. Drums should not be filled or emptied within the storage area.

On-site transportation

Whilst drums containing flammable liquids can be transported securely on a simple pallet, cylinders and drums containing compressed or liquefied gases require special care and appropriate means of transport such as cylinder trolleys or purpose designed attachments for fork lift trucks should be used at all times. The operator should maintain records demonstrating that personnel involved in the movement of drums and cylinders have received training in the hazards involved in handling them and in the operation of any machinery involved such as cranes and fork lift trucks.

Connection and discharge to process

Drums containing flammable substances should be adequately earthed prior to discharge. All containers should be secured in position before connection to process plant. A procedure should be in place for making the connection and all employees should have received adequate training in the use of the procedure. The materials used in making the joint, such as gaskets and lubricants, should be strictly controlled and an appropriate leak test should be carried out when the joint has been made. The pipework that the container is connected to should be designed to an appropriate standard.

Design and maintenance of containers

Drums and cylinders should be designed and constructed to an appropriate standard. The operator should be able to demonstrate that an appropriate inspection and maintenance programme is in place in accordance with the relevant Regulations.

The Regulatory framework is complex with parallel regulations currently being applied. As such, periodic inspection should be done at appropriate intervals as required by regulations or, where inspection is in accordance with TVPR, at the intervals specified in RID and ADR (European Directives covering transport of dangerous goods by rail and road).

Containment of spills

Suitable precautions should be in place for the containment of leaked materials. Where liquids are handled suitable spillage containment such as bunding and drainage sumps should be in place. Arrangements should be in place for the routine drainage of rainwater from sumps. Where materials that react with water are stored outdoors, the operator's risk assessment should demonstrate the suitability of the arrangements. For the storage of toxic gases, location of the containers in a purpose designed indoor store will reduce the rate at which gas is released to the environment.

Control of ignition sources

Where flammable liquids or gases are stored, the area should be subject to hazardous area classification for the control of ignition sources. This requirement should be reflected both in the equipment installed and in the control of operational and maintenance activities in the location. The movement of drums and cylinders often involves the use of forklift trucks, which can provide a source of ignition for flammable vapours. Any vehicle operating in a zoned area should be protected to an appropriate standard.

Chlorine cylinders

The vast majority of chlorine cylinder and drum stores are located indoors and should be solely used for storing chlorine. Access doors should fit closely to help contain any leak. These stores should be protected from any nearby radiant heat hazards. The store should be at least 5 m from any roadway. A cylinder store should be at least 20 m from the site boundary and a drum store 60 m. Chlorine gas detectors / alarms should normally be provided.

Risk assessments should be carried out to consider hazards arising from mishandling (dropping of containers in transport/handling), incorrect operation of valves and failure to connect correctly, maintenance errors and damage by external sources (domino, vehicle impacts, etc.)

Emergency Response/ Spill Control

The technical measures set down below are intended to provide additional detail on the measures that should be considered in plant design and operational procedures.

Safety management systems

Generation and implementation of effective emergency response and spill control procedures are fundamental aspects of a safety management system.

Site emergency plan

The on-site emergency plan should address procedures for dealing with emergency situations involving loss of containment in general terms. In brief, the main points for inclusion are:

- Containing and controlling incidents so as to minimise the effects and to limit danger to persons, the environment and property;
- Implementing the measures necessary to protect persons and the environment;
- Description of the actions which should be taken to control the conditions at events and to limit their consequences, including a description of the safety equipment and resources available;
- Arrangements for training staff in the duties they will be expected to perform;
- Arrangements for informing local authorities and emergency services; and
- Arrangements for providing assistance with off-site mitigatory action.

The emergency plan should be simple and straightforward, flexible and achieve necessary compliance with legislative requirements. Furthermore, separate on-site and off-site emergency plans should be prepared.

Emergency operating procedures / training

The emergency procedures should include instructions for dealing with fires, leaks and spills. The procedure should describe how to:

- Raise the alarm and call the fire brigade;
- Tackle a fire or control spills and leaks (when it is safe to do so);
- Evacuate the site, and if necessary nearby premises.

Area evacuation

Evacuation of areas in the event of fire or toxic gas emission should be addressed in an emergency evacuation procedure. This should specify designated safe areas, assembly points and toxic gas shelters. The procedure should also identify responsible personnel whose duties during area evacuation include:

- Responsibility for a specific area;
- Collecting ID badges from plant racks;
- Ensuring roll calls are undertaken to identify missing persons;
- Communication of missing persons to central emergency services.

Fire fighting

A firefighting strategy should consider:

- Appointment of fire wardens, with subsequent training;
- Location plans of fire hoses, extinguishers and water sources;
- Access for emergency services;
- Provision of firewater lagoons.

Removal of substance to safe place
The emergency spill control procedure should include the following key sections:

- Spills involving hazardous materials should first be contained to prevent spread of the material to other areas. This may involve the use of temporary diking, sand bags, dry sand, earth or proprietary booms / absorbent pads;
- Wherever possible the material should be rendered safe by treating with appropriate chemicals (refer to Stabilisation / dilution to safe condition);
- Hazardous materials in a fine dusty form should not be cleared up by dry brushing. Vacuum cleaners should be used in preference, and for toxic materials one conforming to type H (BS 5415) should be used;
- Treated material should be absorbed onto inert carrier material to allow the material to be cleared up and removed to a safe place for disposal or further treatment as appropriate;
- Waste should not be allowed to accumulate. A regular and frequent waste removal procedure should be adopted.

Stabilisation / dilution to safe condition
Once the hazardous material has been contained to prevent spread of the material to other areas, the material should be treated wherever possible to render it safe. Acids and alkalis may be treated with appropriate neutralising agents. Due to the differing properties of the various groups of chemical, an appropriate treatment strategy with suitable chemicals should be established in each case. For example, highly concentrated hydrochloric acid will fume when spilled so prior to neutralisation the spill should be diluted with a water spray.

Once the material has been treated the cleared up the area should be washed with large volumes of water. Most chemical plants and associated areas are serviced by chemical drains that feed to the effluent treatment plant. The washing operation will represent an abnormal loading on the effluent treatment plant, and it is vital that in any situation where this is likely to happen the staff responsible for operation of the effluent treatment plant are notified so that appropriate measures can be adopted. The effluent treatment plant operatives are likely to require the following information:

- Approximate quantity of hazardous material;
- Approximate composition of hazardous material;
- Physical properties of hazardous material;
- State of hazardous material (whether neutralised etc.).

In the case of fire water run-off, much larger volumes of water are employed and the provision of firewater lagoons to contain potentially toxic firewater is required.

Availability of neutralising substances / foam

Process specific emergency spill kits (acid, alkali, solvent, toxic etc) and appropriate personal protective equipment should be readily available with supporting procedures. These spill kits should be maintained on a regular basis to ensure that they are always available and fit for purpose. This ensures that the most appropriate measure is at hand to deal with a spill or fire in the most effective way.

Issues that should also be addressed include:

- Containment;
- Maintenance and condition of fire hoses, extinguishers.

4.3 Section 3 – SOL-REC2 processes

The potential SOL-REC2 processes all share a common theme of pre-treatment, leaching followed by separation/ dissolution and finally recovery which have been treated as distinctly separate process elements. At this stage of the project, the exact treatment stages have not yet been accurately defined. All potential risks with reference to any pilot plant design, build and operation should be covered within the HAZOP/ HAZID and HAZOP Conformity Measures set down within this report. All matters relating to chemical storage and handling will be as per the Material Safety Data Sheets (MSDS).

However, there are a number of common potential risks that are identifiable at an early stage and these are:

Process		**Risk**	**Likelihood (L/M/H)**	**Impact (L/M/H)**	**Mitigation**
All	Experimental set up	Chemical dust exposure	M	M	Weighing/ mixings in fume cupboard
	Overheating	Generation of harmful volatiles e.g. HCl from PVC	L	M	Cooling
	Chemical leakage	Health hazard, risk to the environment	L	H	Operators to wear protective clothing – ref MSDSs and Ref: HAZOP and HAZOP conformity measures (H and HCM)
Leaching Dissolution	Organic solvents and Ionic Liquids	Leakages	L	H	Ref: HAZOP and HAZOP conformity measures (H and HCM)
	Overheating	Exothermic reaction	M	H	Ref: HAZOP and HAZOP conformity measures (H and HCM)
All	Chemical spillages	Environmental impact	M	M	Bund experimental area and Ref: HAZOP and HAZOP conformity measures (H and HCM)
All	Plant Operating	Operational faults	L	M	Issued documentation and training. Also, Ref: HAZOP and HAZOP conformity measures (H and HCM)

	Plant operation	Start-up problems	L	M	Follow Issued documentation: Ref: HAZOP and HAZOP conformity measures (H and HCM)
	Plant operation	Plant Failures	M	M	Attention to training, maintenance, start-up and general operational procedures; Ref: HAZOP and HAZOP conformity measures (H and HCM)
	Alarm failures	Plant operating incorrectly	L	M	Shut plant down; attention to alarms under maintenance procedures; Ref: HAZOP and HAZOP conformity measures (H and HCM)

5 Overall Summary and Conclusions

The Sol-Rec2 process has been developed to provide a new and highly innovative process for the recovery and recycling of polymers and other materials from complex, mixed material packaging used to protect food and medicines. To date, it has not been possible to recycle these materials in a way that enables individual polymers to be separated and recovered in an economically viable manner. The Sol-Rec2 process uses a unique combination of mechanical and chemical processes that use both established and new technologies to isolate and recover individual materials so that they can be reused. There are many aspects of the overall process that have the potential to generate environmental, health and safety (EHS) issues if not operated in an appropriate optimised way. This deliverable has attempted to provide a general overview and discussion of the important aspects of the process that could present problems during operation. It also provides guidance for those developing and operating the process equipment in order to avoid environmental health and safety issues. It has also provided very detailed information that is specifically focused on the risk assessment and minimisation when developing and operating the type of pilot plants needed for the Sol-Rec2 process. Additionally, there is consideration of the potential risks to both society and the wider environment that could occur during operation of the process e.g. the emission of noxious gases and the generation of non-recoverable waste.

At the time of writing, some of the information provided herein remains rather generic as the project has only just completed the first year of its three-year duration. Consequently, some of the specific details around each of the process stages and the choice of equipment, chemicals and utilities are still to be confirmed. It is likely that there will be ongoing refinement and optimisation throughout the remainder of the project. This current version of the deliverable should be considered as covering the Sol-Rec2 process as it is currently understood at the end of July 2022. It is the intention of the authors to provide additional periodic updated versions of the deliverable as more information becomes available and to issue a final version towards the end of the project when the Sol-Rec2 process is more accurately defined.

6 Sources of Further Useful Information and Guidance

The UK Health and Safety Executive have produced numerous guidance documents that provide useful detailed information specific to plastics recycling operations and a selection of pertinent examples are listed below.

- **Safety at injection moulding machines PPIS4(rev1) 2015 (PDF)**
  Revised guidance (first published in 1999) outlines practical safeguards to reduce the risk of injury at injection moulding machines.

- **Safety at extruder lines PPIS7(rev1) 2015 (PDF)**
  Revised guidance (first published in 1999) outlines practical safeguards to reduce the risk of injury at extruders

- **Safety at granulators PPIS10(rev1) 2015 (PDF)**
  Revised guidance (first published in 1998) to align with Dangerous Substances and Explosive Atmospheres Revised guidance (first published in 1999) outlines practical safeguards to reduce the risk of injury at granulators 2002

- **Controlling fumes during plastics processing PPIS13(rev1) 2013 (PDF)**
  Updated guidance (first published in 2002) on how to prevent or control any respiratory and toxic hazards from fume produced by plastics processing

- **A workers' pocket guide to local exhaust ventilation (LEV)**
  Published in 2008, this is a pocket card for employees working in jobs that produce airborne dust, mist, fumes or gas. It alerts them to the fact that they need to check any local exhaust ventilation (LEV). It contains a daily checklist to make sure it is working properly so that they can protect their health.

Other useful documents are as follows;

- **Plastics and rubber machines - Extruders and extrusion lines - Part 1: Safety requirements for extruders. European Standard EN 1114-1:2011.**

This European Standard specifies all significant hazards, hazardous situations and events relevant to all types of screw extruders for plastics and rubber, when they are used as intended and under conditions of misuse which are foreseeable by the manufacturer.

- **Commission Regulation (EC) No 282/2008 of 27 March 2008 on recycled plastic materials and articles intended to come into contact with foods and amending Regulation (EC) No 2023/2006**

- **Overview of known plastic packaging-associated chemicals and their hazards**
  Ksenia J. Groh, Thomas Backhaus, Bethanie Carney-Almroth, Birgit Geueke, Pedro A. Inostroza, Anna Lennquist, Heather A. Leslie, Maricel Maffini, Daniel Slunge, Leonardo Trasande, A. Michael Warhurst, Jane Muncke, Science of The Total Environment, Volume 651, Part 2, 2019, pp3253-3268, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2018.10.015 (accessed 05/07/22)

- **Controlling fumes during plastics processing**
  Published by the Health and Safety Executive, PPIS13 (rev1), 2013. Available for download from; https://www.hse.gov.uk/pubns/ppis13.pdf (accessed, 05/07/2022).

- **Hazardous substances in plastics – ways to increase recycling**
  Åsa Stenmarck, Elin L. Belleza, Anna Fråne, Niels Busch, Åge Larsen and Margareta Wahlström (2017)
  ISBN 978-92-893-4848-5 (print) ISBN 978-92-893-4849-2 (pdf) ISBN 978-92-893-4850-8 (EPUB)
  http://dx.doi.org/10.6027/TN2017-505 (accessed 07/07/22)

- **Acetic Acid Hazards: How to Ensure Safety Handling the Chemical**
  (2019)
  https://freechemistryonline.com/acetic-acid-hazards-how-to-ensure-safety-handling-the-chemical (accessed 07/07/22)

- **VOC emissions form waste plastics during melting processes**
  Yamashita, K. & Kumagai, Kazukiyo & Noguchi, Miyuki & Yamamoto, Naomichi & Ni, Y. & Mizukoshi, Atsushi & Yanagisawa, Y. (2007).
  The 6th International Conference on Indoor Air Quality, Ventilation & Energy Conservation in Buildings IAQVEC 2007, Oct. 28 - 31 2007, Sendai, Japan.
  https://www.aivc.org/resource/voc-emissions-waste-plastics-during-melting-processes (accessed 07/07/22)

- **Ionic Liquids Toxicity—Benefits and Threats**
  Jolanta Flieger and Michał Flieger
  Int. J. Mol. Sci. 2020, 21(17), 6267
  https://doi.org/10.3390/ijms21176267 (accessed 07/07/222)

- **Emerging impacts of ionic liquids on eco-environmental safety and human health.** Wei, Penghao & Pan, Xiujiao & Chen, Chien-Yuan & Li, Hsin-Yi & Yan, Xiliang & Li, Chengjun & Chu, Yen-Ho & Yan, Bing.
  Chemical Society Reviews, 50, 13609-13627 (2021)
  https://doi.org/10.1039/D1CS00946J (accessed 07/07/22)

7 Sources of Material Safety Data Sheets (MSDS)

(All sources accessed 19/07/22)

Acetic (ethanoic) Acid

https://www.fishersci.co.uk/store/msds?partNumber=10620131&productDescription=500ML+Acetic+acid+glacial%2C+pure%2C+aldehyde+free&countryCode=GB&language=en

https://www.sigmaaldrich.com/AU/en/sds/sial/537020?sdslanguage=EN

https://fscimage.fishersci.com/msds/00120.htm

http://sds.chemtel.net/webclients/safariland/finished_goods/Pioneer%20Forensics%20-%20PF001%20-%20PF002%20-%20Acetic%20Acid%20-%20Glacial.pdf

http://www.labchem.com/tools/msds/msds/LC10100.pdf

Propionic Acid

https://beta-static.fishersci.com/content/dam/fishersci/en_US/documents/programs/education/regulatory-documents/sds/chemicals/chemicals-p/S25508.pdf

https://www.sigmaaldrich.com/GB/en/sds/ALDRICH/W292419

https://www.merckmillipore.com/GB/en/product/Propionic-acid,MDA_CHEM-800605

https://www.brecklandscientific.co.uk/v/vspfiles/MSDS/S8001614.pdf

https://www.perstorp.com/-/media/files/perstorp/msds/propionic%20acid/msds_propionic%20acid_engca-6753.pdf

Butyric (Butanoic) Acid

https://www.sigmaaldrich.com/GB/en/sds/aldrich/b103500

Decanoic Acid

https://www.sigmaaldrich.com/GB/en/sds/sigma/c1875

Thymol

https://www.sigmaaldrich.com/AR/en/sds/sigma/t0501

https://www.fishersci.com/store/msds?partNumber=T185100&productDescription=THYMOL+NF+100G&vendorId=VN00033897&countryCode=US&language=en

https://www.finarchemicals.com/msds/Thymol%20crystals.pdf

https://www.cdhfinechemical.com/images/product/msds/19_193987441_Thymol(Crystal)-CASNO-89-83-8-MSDS.pdf

https://www.oxfordlabchem.com/msds/(T-08950)%20THYMOL%20CRYSTAL%20Extra%20Pure.pdf

1-Methylimidazole

https://www.sigmaaldrich.com/GB/en/sds/aldrich/m50834

1-Ethylimidazole

https://www.sigmaaldrich.com/GB/en/sds/aldrich/690147

Pyridine

https://www.alfa.com/en/msds/?language=EN&subformat=AGHS&sku=19378

4-Methylpiperidine

https://www.sigmaaldrich.com/GB/en/sds/aldrich/m73206

N,N-Dimethylbenzylamine

https://www.sigmaaldrich.com/GB/en/sds/aldrich/185582

Trioctylamine

https://www.sigmaaldrich.com/GB/en/sds/aldrich/t81000

N-methylmorpholine

https://www.sigmaaldrich.com/GB/En/sds/Aldrich/M56557

Acetone

https://www.sigmaaldrich.com/GB/pt/sds/sigald/179124

Ethanol

https://www.sigmaaldrich.com/GB/en/sds/sial/459836