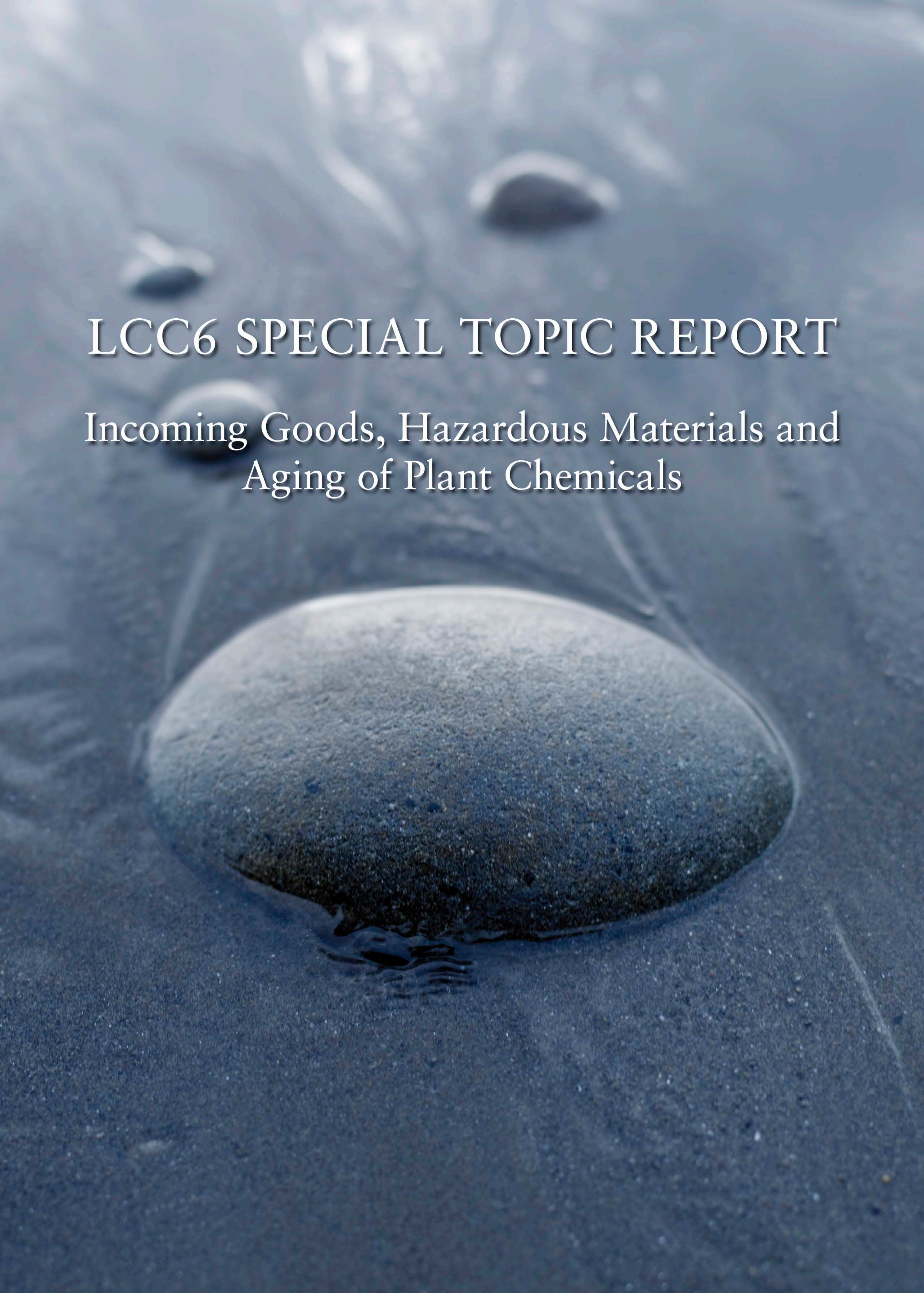

LCC6 SPECIAL TOPIC REPORT

Incoming Goods, Hazardous Materials and Aging of Plant Chemicals

Incoming Goods, Hazardous Materials and Aging of Plant Chemicals

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Contents

1 Introduction (Hartmut Venz)

In Nuclear Power Plant (NPP), chemicals and materials are used in various aspects like power production, equipment maintenance, water treatment, waste treatment, and chemistry laboratories. A lot of chemicals and substances used have a limited lifetime and may contain impurities. The concentration of impurities has to be low enough to exclude both local corrosion problems as well as minimizing their possible activation to radio nuclides with undesired high radiation. The staff should understand the use of individual chemicals and materials, the flow of those chemicals through their facilities, and the options for changing those chemicals or materials to reduce the risk of corrosion and environmental impact, to ensure safety and health, to improve compliance and reporting efficiency and to minimize costs.

For that reasons it is necessary to pay enough attention to the selection and acquisition of chemicals, to their storage, transport or movement through facilities, or to the disposition of spent chemicals. Another important point is to have a reliable system to manage all the needed information, a so-called chemical information management system which addresses all parts of the process starting with selection, and ending with waste disposal. Between these tasks, an incoming goods inspection and an aging management should be of special interest.

In particular, for a NPP it is very important to know and to take into account the numerous laws, regulations, and procedures as introduced in Chapter 3.

2 Reasons for an incoming goods program - example of the French approach (Francis Nordmann)

2.1 Overall principle

The French principle of controlling incoming goods is mainly based on a preventive approach which means using a quality assurance system that is defining *a priori* that the materials will cope with the expectation instead of *a posteriori* controlling that what is provided is matching the corresponding specification.

The French organisation has been established in 1990 under the PMUC acronym which stands for "*Produits et Matériaux Utilisables en Centrales*" i.e. Products and Materials that can be used in NPP.

It is mandatory for components that are important for safety but is also advisable for other components. Moreover, it looks reasonable to only have one type of product in the plant to avoid any error.

2.2 Reason for the limitation

The PMUC organisation is applied for several purposes:

- Avoiding the corrosion risk of metallic components,
- Ensuring safety of the staff using or manipulating the products and chemicals,
- Mitigating toxicological aspects,
- Considering the production of wastes and the environmental impact.

The presence of element that may be highly activated has not originally been included in this PMUC approach but must obviously be taken into account to avoid for example cobalt, silver, antimony.

Corrosion purpose is at the origin of controlling the use of materials, chemicals and incoming goods in NPP due to the important degradation that occurred in the past or even more recently in some NPP.

For example, in the 1970s, several cases of pitting have been observed on brand new components, in France, Belgium, etc. More recently, pitting occurred on steam generator tubing of Taiwan NPP due to the presence of chloride associated to a poor environment of the component shipped from Russia to China [Wang, 2006].

2.2.1 Corrosion risk

Although stainless steel or other alloys resistant to corrosion are used for the primary coolant as well as many other components of the other systems in the plant, there are several types of corrosion that may occur due to the presence of some elements on the metallic surfaces of components. The corrosion may either develop at room temperature, under lay-up condition, or be enhanced when the component is operating at higher temperature, which is particularly true for corrosion phenomena dependant on the temperature, like Stress Corrosion Cracking (SCC). On the opposite, pitting may develop even at low temperature under poor chemical environment.

The various types of corrosion may appear in a liquid (or humid) environment and in presence of detrimental chemical elements, particularly oxidizing environment (presence of oxygen from air) or some specific pollutants, such as halides (chloride, fluoride, bromide), sulphur compounds (especially the reduced compounds of sulphur i.e. sulphides, sulphites, thiosulphides, thiosulphites) even more easily in acidic environments.

Chlorides or reduced compounds of sulphur are very detrimental while sulphates do not have the same noxiousness when present in some products entering in contact with metallic surfaces.

Figure 2-1 is showing the combined influence of chloride concentration and temperature on SCC of stainless steel [Combrade, 2010].

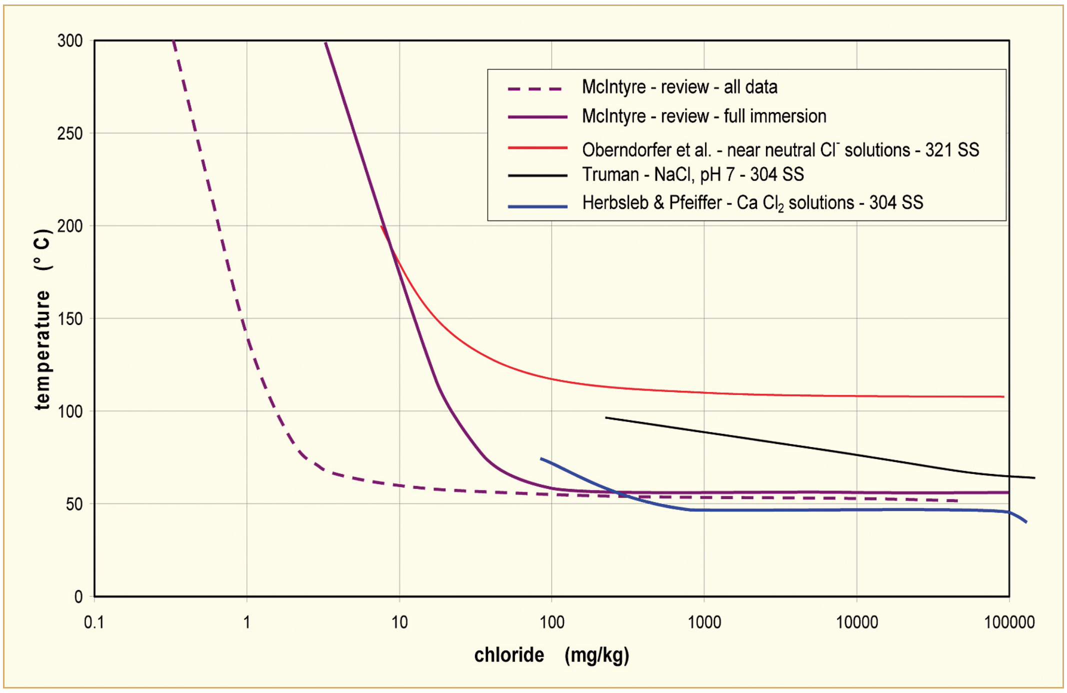

Figure 2-1: Influence of chloride and temperature on SCC of stainless steel [Combrade, 2010].

The main degradations observed on the turbine of the Electricité de France (EdF) fleet have been concerning studs (bolts) in High Pressure turbine of 900 MW units [Dordonat, 2006]. Penetrating oils used during disassembly of stud/bolts associated with residues of high-pressure drilling were containing products with chlorine. SCC observed on stud/bolts broken after 15 000 h in September 1983, came from the presence of chloride in water at 250 °C on a material with high tensile stresses.

Corrosion of Low Pressure rotor disks occurred on zones with high stresses in an acidic environment containing sulphur (thermal decomposition of MoS_2). Disk 4 and 11 are the first to be wet since they are just after the pressure reducing line. Products lixiviated by condensed steam concentrate in dead zones and cracking occurs when the contaminated environment becomes sufficiently acidic on a sensitive steel (26 NVC 11-6, a low alloy steel with 0.26 % C, containing 2.75 % Nickel; 0.6 % Vanadium and some chromium) in presence of high stresses (350 MPa at the reaming location).

Besides the serious SCC damages that may be induced by the presence of chloride on stainless steels, this anion is also at the origin of pitting in oxygenated environment.

Pitting may easily occur in aerated environment in presence of chloride, fluoride in a lesser extent, or sulphur compounds. The degradation depends on the concentration in chloride, the temperature, the pH. Pitting increases when temperature and pH decrease and when chloride content increases, as shown on Figure 2-2.

3 Legal requirements (Hartmut Venz)

With regard of the use of chemicals and materials in NPP, the following laws, regulations and procedures are important. These legal documents may be different in several countries. However, for all member states of the European Community (EU) it is mandatory to adapt the laws into their national ones. Most countries edited chemical acts and ordinances on hazardous substances. The latest issues of these take into account the newest European regulation No 1907/2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), which was issued on 18 December 2006 [Regulation 1907 (EC), 2006].

The new system of classification and labelling of chemicals was edited by the United Nations Economic Commission for Europe (UNECE). As of 2010, the second revised edition is valid and published on the homepage of the organisation [UN[1], 2007].

All operators of NPP should take into account most of the following laws, ordinances and documents:

- Chemical act and ordinance
- Ordinance on hazardous substances
- REACH (Registration, Evaluation and Authorization of Chemicals)
- GHS (Globally Harmonized System of Classification and Labelling of Chemicals)
- International Atomic Energy Agency (IAEA) Safety Guide (Draft) DS 388 "Chemistry Program for Water Cooled Nuclear Power Plants"
- Statutory order on hazardous incidents (not subject of this paper)
- Labour protection laws (not subject of this paper)
- ADR/RID (Transport regulations) (not subject of this paper)
- VOC-Ordinance (Volatile Organic Compounds) (not subject of this paper)

3.1 Chemical act

The Chemical Law shall avoid harmful influences of dangerous materials and substances on:

- The environment,
- human health and
- the employees when dealing with dangerous materials.

Quintessential points of the chemical act [Federal Law, 1998] in Germany and the corresponding set of rules based on it are:

- Evaluation of the risks by an extensive examination in the announcing and report procedure for new materials, which were brought on the market for the first time after 1981. The risk evaluation of old materials takes place by a valid European Economic Community (EEC) regulation directly in all EEC member nations.
- Marking of the dangerous material properties, in order to make responsible handling possible, by classification, labelling and packing of chemicals. Further details are regulated in the regulation on hazardous substances by reference to EEC-legal regulations [Federal Law, 2004].
- Preventing report obligations of the industry about composition of certain chemicals.

[1] United Nations

- Prohibitions and restrictions for a certain catalogue of chemicals are in the chemical prohibition regulation, and production and use of the chemicals are concerned in the regulation on hazardous substances.

- Regulations to the so-called Good Laboratory Practice which are to guarantee the reliability and the comparability of material examinations.

3.2 Ordinance on hazardous substances

- The regulation on hazardous substances in Germany [Federal Law, 2004] shall apply to the placing on the market of substances, preparations and products for the protection of employees and others against threats to their health and safety by dangerous substances and to protect the environment from chemical-related impact.

- A substance or preparation shall be classified as hazardous insofar as it possesses one or more of the properties referred to in article 3a of the chemicals act and as defined in greater detail in Annex VI of directive 67/548/EEC. This dangerous substances directive is one of the main European Union laws concerning chemical safety. The last version has the number directive 1999/33/EG.

- According to the directive, a substance or preparation shall be defined as:

1) Explosive where, in a solid, liquid, pasty or gel state, it has the capacity to react exothermically and rapidly generate gases with or without the presence of air, and under defined test conditions either detonate, deflagrate or upon heating explode when partially confined.

2) Oxidizing where, though the substance or preparation is not as a rule inherently combustible, the risk of fire and the intensity of any fire are greatly increased by contact with any flammable substance or preparation, mainly through the release of oxygen.

3) Extremely flammable insofar as the substance or preparation:
    - Has an extremely low flash and boiling point in a liquid state;
    - have explosive limits when mixed with air in a gaseous state under normal temperature and pressure conditions.

4) Highly flammable insofar as it:
    - Becomes hot and can ultimately ignite in air under normal temperature conditions without any energy input;
    - while in a solid state is potentially highly flammable after brief contact with an ignition source and continues to burn or to be consumed hazardously after removal of the ignition source;
    - has a very low flash point in a liquid state;
    - generates hazardous quantities of extremely flammable gases upon contact with water or damp air.

5) Flammable insofar as it has a low flash point in a liquid state.

6) Highly toxic insofar as it causes death or is acutely or chronically deleterious upon being absorbed through the skin, inhaled or swallowed in minute amounts.

7) Toxic insofar as it causes death or is acutely or chronically deleterious upon being absorbed through the skin, inhaled or swallowed in minute amounts.

4 Management of chemicals and hazardous materials (Hartmut Venz)

A life cycle of a chemical or material used in a NPP consists of several steps:

- Selection and requirement,
- acquire the chemicals according to the needed quality,
- receive the chemical and material and check their compliance with the specifications,
- manage storage, transport, and distribution,
- ensure correct use of the chemicals and materials,
- management and release of the used chemicals and materials, and
- reporting and documentation.

To manage the numerous activities mentioned above, a sufficient data base and a management system should be available. This could help the different managers in the plant, who are responsible for operation, maintenance, and chemistry, as well as environmental managers, stores managers, and purchasing personnel.

The chemical data management system should be compatible with existing plant data management systems and accessible in any of several forms: paper files, electronic spreadsheets, electronic databases, or custom electronic applications. With an easy access to this information, plant staff will be able to improve decision-making where chemicals and materials are concerned as well as simplify reporting and to ensure the regulatory compliance.

Ideally, a management system combines the different processes like purchasing, approval, quality assurance, and protection of health and environment [Lehmann et al, 2010]. The data and processes concerning procurement are connected to the material specific databank by means of a SAP database system. The user can completely answer all questions concerning the quality, applications and operational safety of materials. All users of the plant services computer network have access to all relevant documents associated with hazardous materials while they are filling in work permit forms or scheduling work. Moreover, the system enables a companywide standardized labelling of material containers due to the corporate classification categories.

4.1 Detail processes of a management system

On one hand, in order to develop such a management system, all identified activities that occur during each life cycle stage and the information generated about a chemical at each point have to be taken into account. On the other hand, different legal requirements, conditions to protect employees as well as components and materials of the plant have to be considered as shown in Figure 4-1.

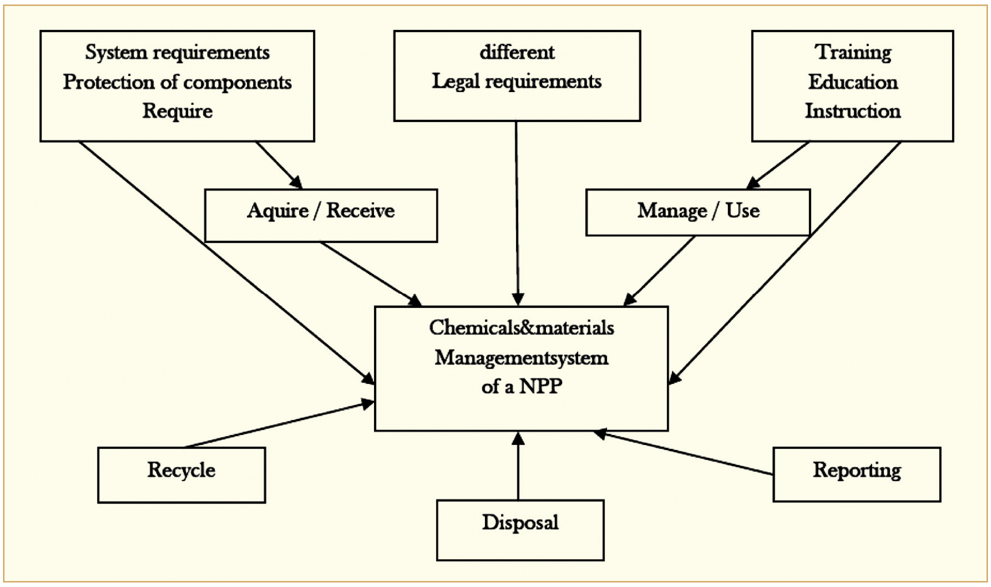

Figure 4-1: Processes considered in a management system for chemicals and hazardous materials.

4.1.1 Require chemicals and hazardous materials

The utility personnel need both information about chemicals and material used and their flow in the plant. The first step in a chemical life cycle is to identify the need for a chemical. At this stage, someone at the planning or use level identifies the need for a chemical to perform a certain task. This person may work with engineering, purchasing, stores, and/or the environmental staff to verify the need and/or to develop appropriate specifications.

At some stations the work is done by a special task force or working team. Figure 4-2 presents the overall map of activities and data for identifying a chemical need. Information developed at this stage includes the user name, the process requiring the chemical, and the required specifications. It may also include required quantities, anticipated use rates, anticipated waste characteristics and quantities, and general health and safety considerations.

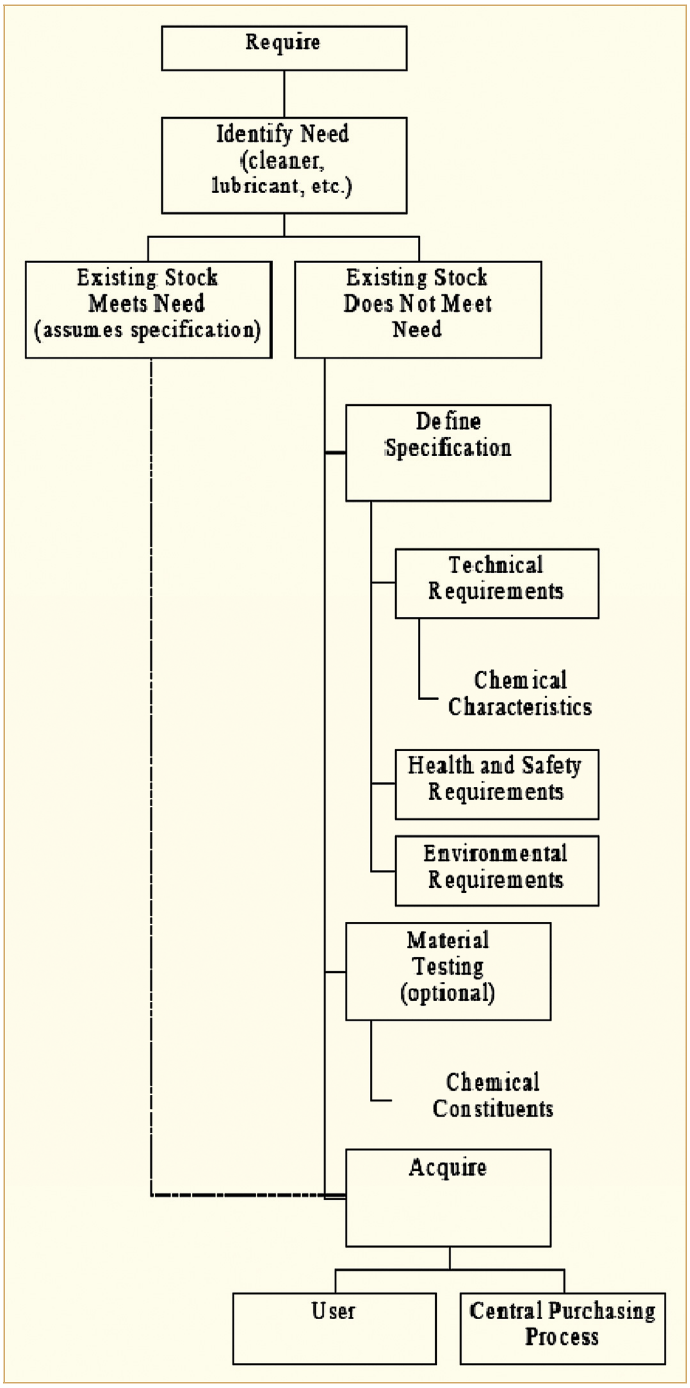

Figure 4-2: Tasks to require a chemical or material [Murray et al, 1999]. (Boxes indicate activities. Information or data are shown without boxes.)

4.1.2 Acquire chemicals and hazardous materials

If a new product is required, the user may compile a list of potential products and review them with engineering, environmental, and/or the health and safety staff to identify products that meet the user's technical needs. Figure 4-3 presents the overall map of activities and data to acquire a chemical.

Information that is developed at this stage includes the list of potential products; evaluation criteria and results, the selected product name, associated vendor information, quantity and container size ordered, and cost.

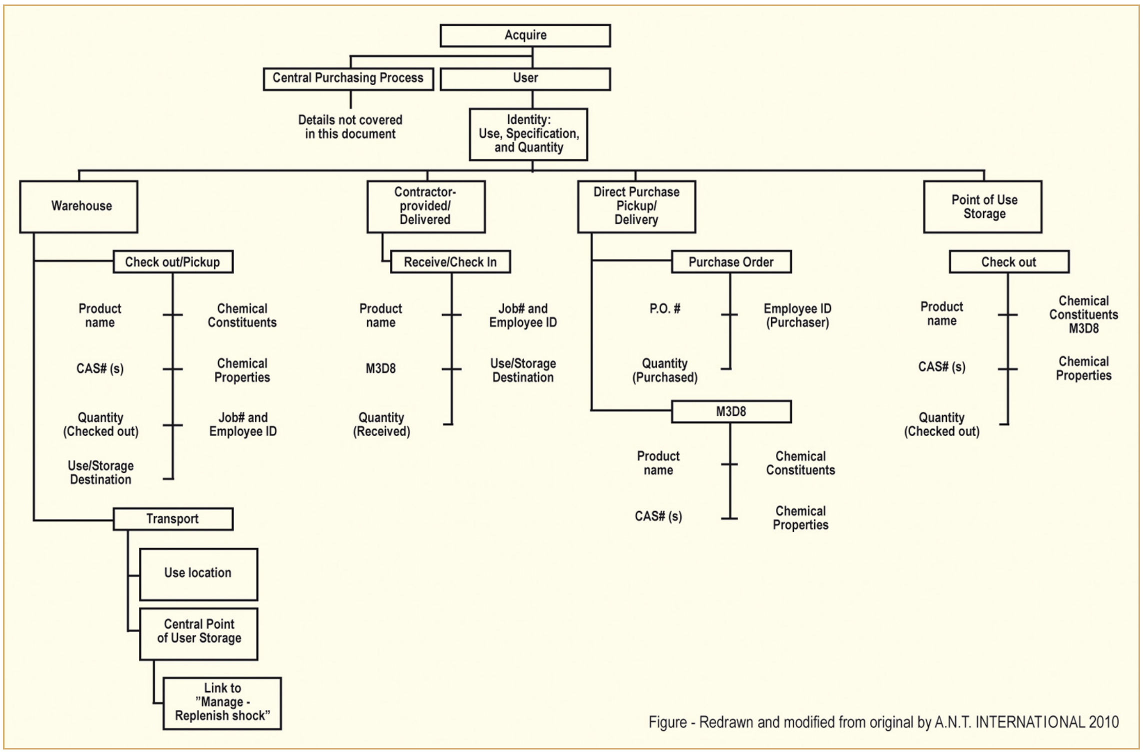

Figure 4-3: Activities and data to acquire a chemical [Murray et al, 1999]. (Boxes indicate activities. Information or data are shown without boxes.)

4.1.3 Receive of chemicals and hazardous materials

When the vendor or transporters deliver the product to the site, typically the shipment is unloaded and inspected for its condition and consistency with the order. The store's manager may then sign the receipt and file a copy of it. Figure 4-4 presents the overall map of activities and data for the receipt of a chemical. Information available at this stage includes the product name; vendor or transporters information, quantity and date received, location received, container size and type, cost, and- very important- the MSDS.

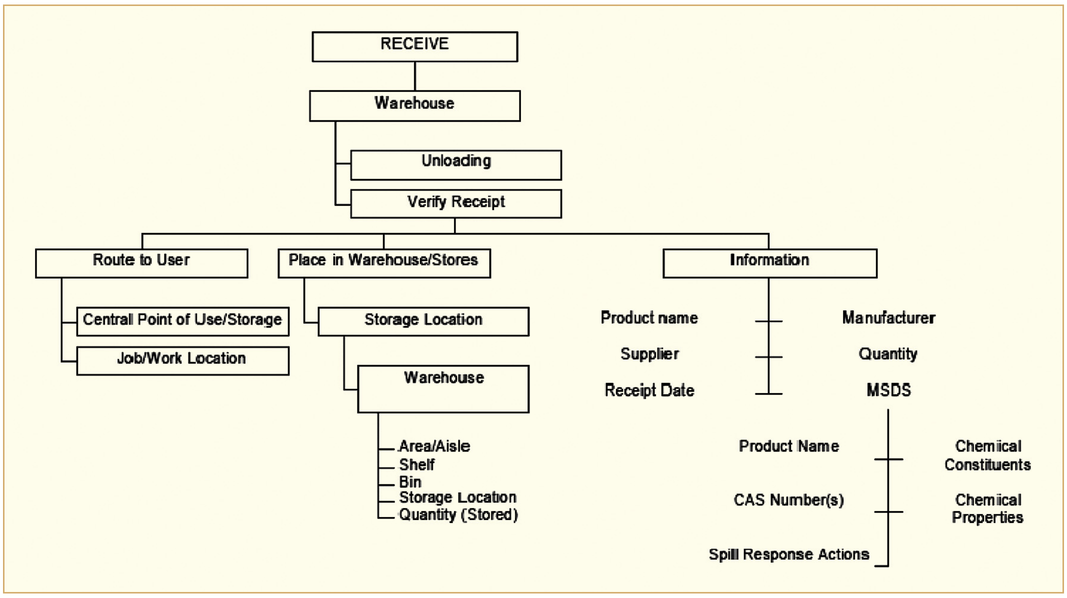

Figure 4-4: Activities and data for the receipt of a chemical [Murray et al, 1999]. (Boxes indicate activities. Information or data are shown without boxes.)

4.1.4 Handling, managing, and use of chemicals and hazardous materials

After accepting the product on site, it is placed into the storage, recorded into inventory, the Material Safety Data Sheet (MSDS) is discarded, and user is informed that it is available.

Information available at this stage includes product name, storage location, quantity in stock, quantity issued, cost of the quantity issued, employee and department to whom the material was issued, MSDS, and special handling or storage requirements that may be associated with the product.

The term "use" describes any application or utilization of a chemical product. Identifying the specific uses and points of use of chemical products is an important stage in defining the life cycle of a chemical. Many of the benefits to be derived from a chemical life cycle management program are associated with identifying specific chemical uses and points of use.

As personnel use chemical products while conducting their various responsibilities, they will evaluate the performance of the product and decide whether it is acceptable or whether they should return it to stores and choose another previously identified potential product.

Not all utilities routinely evaluate the effectiveness of specific products or gather data to evaluate potential product substitution alternatives to save money through acquisition, special use requirements, or waste management. In some cases, an employee may use a product "off the shelf," regardless if it is ideally suited to the activity, to save time and/or money. Information on product performance and suitability collected from users and evaluations of specific-use applications can be valuable in identifying products that are candidates for replacement.

5 Quality control of incoming goods and materials (Wilfried Rühle)

The potential harmfulness of chemicals used in NPPs depends on the location and the modality the products shall be used in the plant.

The highest relevance is concerning chemicals used in safety related systems or those influencing the availability of the plant. These are predominantly the reactor cooling systems, the balance of the plant and important auxiliary systems. Hereby a special importance is connected to chemicals, which can be exposed to the reactor coolant and the water and steam within the balance of the plant, such as Dry Film Lubricants and Operational Chemicals. Reasons for that is their corrosion potential or their activation in the neutron field of the reactor (product group 1).

A difference in their harmfulness is concerning products that are potentially corrosive but cannot and must not come into contact with primary coolant and high purity water and steam. If these products have to be used during shutdown, maintenance or during the construction of systems within the inner surfaces of components, they have to be completely removed before start-up. All the products (product group 2) used for non-destructive tests belong to this category.

A separate category is potentially corrosive products used for safety related components, but individually and not routinely used (product group 3).

All other chemicals used at the plant, which cannot come into contact with reactor components, the balance of the plant, or other safety related systems, should also be limited and controlled because of different reasons (health protection, legislation, environmental reasons, etc.) (product group 4).

All chemicals, which are not included in one of the three groups, are forbidden on the premises of the plant.

In the following chapters, examples of specifications for chemical products are shown. The products and specifications are only examples based on operational experience of one country, one plant supplier and one NPP-operator. By courtesy of this operator of three PWRs and one Boiling Water Reactor (BWR), the following data can be used. Several decades of save operation of these plants using these specifications ensure the quality and effectiveness of the herein mentioned specifications. Worldwide different approaches are possible and different specifications may be valid as well. Nevertheless, products and specifications used elsewhere should be in the same range (or at least not less restrictive), as the materials and the operational conditions are similar worldwide.

The French approach for controlling incoming goods is described in Chapter 2. The strong experience from the biggest PWR–fleet in the world and the other data proposed by one author of this document should not be mixed up with the following data. Some reiterations cannot be avoided. A separate evaluation of these two approaches may efficiently enable the reader to make his own substantiated decisions.

5.1 Lubricants

5.1.1 Lubricants for construction

For the assembly of plant components lubricants for screws are necessary. In case that the lubricants can come into contact with the coolant (product group 1), narrow limits for pollutants are necessary. The following limitations are suggested:

Table 5-1: Limits for impurities in lubricants with coolant contact (product group 1).

Total Fluorine + Chlorine	Maximum concentration	200	mg/kg
Sulphur	Maximum concentration	200	mg/kg
Lead	Maximum concentration	100	mg/kg
Copper	Maximum concentration	100	mg/kg
Zinc	Maximum concentration	100	mg/kg
Bismuth	Maximum concentration	100	mg/kg
Antimony	Maximum concentration	100	mg/kg
Tin	Maximum concentration	100	mg/kg
Mercury	Maximum concentration	100	mg/kg
Arsenic	Maximum concentration	100	mg/kg
Cadmium	Maximum concentration	100	mg/kg

An order should come out of one batch. Each shipment should be analysed for chlorine, fluorine and sulphur.

After three years of storage, the product should be re-examined by chemical analysis.

5.1.2 Dry film lubricants

These products are made from ultrapure graphite powder, a binding agent and an organic solvent, such as isopropanol or butyl acetate.

These products are permitted for all surfaces in contact with coolant. They reduce friction but do not provide corrosion protection. They can be used for all materials.

Caution: Lubricants on ultra pure graphite powder base must not be mixed with silicone grease.

Contamination with impurities should not exceed the values of Table 5-1.

5.1.3 Metal free pasty and spray able solid lubricants

These are high temperature stable, solid lubricants on zirconium oxide base combined with other solid lubricants in partly synthetic oil. The products are temperature stable up to 1400 °C.

The products are used for screw joints in areas in contact with or without coolant, especially for highly heat resisting alloys with high contents of chromium, nickel or molybdenum.

For some of these products, there are restrictions for their use, e.g. they are not usable for closed small volumes. The data sheets should be followed.

5.1.4 Lubricants for rubber and plastics

Products for these purposes can be silicone grease, which is made from silicone oil and thickeners, or vaseline, a mixture of saturated hydro carbons.

These products are used for o-rings, rubber gaskets and plastic components, such as plastic ball valves etc.

These products must only be applied in thin layers.

Silicon grease must not be used in systems operated at temperatures >220 °C. Silicon grease must never be used in systems containing lube oil or hydraulic control fluid (because of foam formation). It must not be mixed with dry film lubricants.

5.1.5 Film lubricants for surfaces with no coolant contact

To this group belong lubricants for component assembly on molybdenum sulphide base, MoS_2 (product group 3). These products are suspensions of extremely fine MoS_2-particles in organic or inorganic binders and solvents. The organic solvents, free from halogen, evaporate after application and the remaining binder retains the MoS_2-powder on the metal surface and so making a lubricating film.

The impurities in the dried product should be limited. As an example, the following values can be used:

Table 5-2: Limits for impurities in lubricants without coolant contact (product group 3).

Chlorine	Maximum concentration	200	mg/kg
Fluorine	Maximum concentration	200	mg/kg
Lead	Maximum concentration	500	mg/kg
Zinc	Maximum concentration	500	mg/kg
Antimony	Maximum concentration	500	mg/kg
Tin	Maximum concentration	500	mg/kg

These products can be used for austenitic stainless steel, ferritic stainless chromium steel and low or not alloyed steel.

It must not be used for components made from nickel-based alloys.

After two years of storage, the product should be re-examined by chemical analysis.

5.1.6 Silicon oil

Silicone oil is a colourless clear, neutral, hydrophobic and low volatile liquid, with good lubricating property. Its viscosity is only a little temperature dependant, it has good adhesive power and it is heat resistant on air and does not be destroyed to unwanted resin.

5.8 IER

The specifications for this product group were made by analysing many commercial products and finding out the best qualities attainable. By these results, limiting values for ion exchanger quality were established. To verify the identity of the product and the compliance of the purchased products with the specifications, each batch has to be examined. IER belong to product group 1.

5.8.1 Powder resins

Powder resins are predominantly used in BWR for condensate polishing and reactor water purification. They are used to remove radionuclides, such as fission products and corrosion products, ionic pollutions and particulate pollutions.

Table 5-39: Quality specifications for powder resins, reactor quality.

Acetate	Maximum concentrations	100	mg/kg
Chloride	Maximum concentrations	50	mg/kg
Fluoride	Maximum concentrations	2	mg/kg
Formicate	Maximum concentrations	135	mg/kg
Sulphate	Maximum concentrations	100	mg/kg
Settle able flocculating product after 10 min.		160 - 230	ml

The product should be ordered from one batch with a certificate of the producer.

After delivery, the specified parameters should be verified for each batch.

5.8.2 Mixed bed resins for use in the primary circuit

These types of mixed bed resins are used for primary coolant in the auxiliary systems of the reactor and for steam generator blow down.

They are used to remove radionuclides, such as fission products and corrosion products, ionic pollutions and as far as possible particulate pollutions.

Table 5-40: Quality specifications for mixed-bed resins in "Nuclear Grade quality".

Acetate	Maximum concentration	100	mg/kg
Chloride	Maximum concentration	50	mg/kg
Fluoride	Maximum concentration	2	mg/kg
Formate	Maximum concentration	100	mg/kg
Sulphate	Maximum concentration	100	mg/kg
Sieve fraction >125 µm	Maximum value	150	mg/kg
Sieve fraction <125 µm	Maximum value	30	mg/kg

The product should be ordered from one batch with a certificate of the producer.

After delivery, the specified parameters should be verified for each batch.

5.8.3 Cation resins

Cation resins are used in the cooling systems of the generators and in some plants and for steam generator blow down. The same quality should be used as for the mixed bed resins in "Nuclear Grade quality".

Before using the resins it has to be verified, that the resins have been regenerated with acid (H-form).

The product should be ordered from one batch with a certificate of the producer.

If cation resins and anion resins are mixed to get mixed bed resins, the before described specification for mixed bed resins should be followed.

5.8.4 Catalyser resins

Catalyser resins are resins without active groups and coated with the noble metal palladium. They are used for recombination of hydrogen and oxygen in the generator coolant.

The catalyser resins should be free from chloride. The effectiveness of the resin can be tested in the lab by the reaction of oxygen with hydrazine.

The product should be ordered from one batch with a certificate of the producer.

After delivery, the specified parameters should be verified for each batch.

The allowed duration for storage is one year. This time period starts again, if the product is re-qualified by a new test.

5.8.5 Filter aids, inert

Filter aids, such as fibres made from poly acryl nitrile (PAN), are used as protective layers on the precoat layer made with powder resins. Because of operational experience, the product should be free from corrosive ions.

Table 5-41: Impurity specification for filter aids made from PAN.

Chloride (in leach out water)	Maximum concentration	50	mg/kg
Fluoride (in leach out water)	Maximum concentration	50	mg/kg
Sulphate (in leach out water)	Maximum concentration	50	mg/kg

The product should be ordered from one batch with a certificate of the producer.

After delivery, the specified parameters should be verified for each batch.

6 Laboratory chemicals (Hartmut Venz)

In NPP laboratories, many different chemicals, conventional ones and those of very high purity (p.a.) are used. As these chemicals are purchased as specified products, it is not necessary to establish additional plant internal specifications.

The high educated and well-trained staff, chemists as well as laboratory-assistants are familiar with careful handling and storage of chemicals. The advice in Chapter 7 about storage of chemicals and hazardous substances in the warehouse of the plant should also be followed in laboratories.

It should be kept in mind that it is strongly prohibited to use chemicals and hazardous substances for analytical purposes for any other tasks or at any other places in the plant. Only the staff of the laboratory but no other person in the plant is allowed to use laboratory chemicals. Misapply could result in serious problems or incidents.

6.1 Basic principles to handle chemicals in the labs

The amount of chemicals in the laboratories should be sufficient for half a year. A corresponding amount of basic chemicals, standards as well as assigned chemicals should be stored on-site.

All chemicals have to be stored in original packages as long as they are used.

Storage conditions have to be specific for each chemical or substance.

After receiving the chemicals, an entrance check is mandatory. An identification mark with the plant internal expiry date has to be attached.

When the specified expiry date is reached or exceeded, opened and unopened chemicals must be disposed.

It is also important not to exceed limits for burnable and flammable liquids in laboratories, storages and working places.

Exposure of chemicals to heat or direct sunlight should be avoided. Otherwise, this may lead to the deterioration of storage containers and labels, as well as to degradation of the chemicals.

Flammable materials should be stored in an approved, dedicated, flammable materials storage cabinet or room.

Do not simply store chemicals in alphabetical order.

Avoid storage of chemicals on the floor (even temporarily).

Avoid stockpiling chemicals.

Store incompatible chemicals separately according to their hazard class codes, to avoid unwanted reactions.

Liquids should be stored in unbreakable or double-walled containers, or the storage cabinet should have the capacity to contain the total volume of the container.

Chemicals should not be stored higher than eye level and never on the top shelf of a storage unit.

Conduct periodic cleanouts to prevent accumulation of unnecessary chemicals.

A systematic control of the status should be performed in storages as well as in laboratories twice a year.

8 Aging during storage (Wilfried Rühle)

8.1 Introduction

Plant chemicals, predominantly organic chemicals, are generally instable by interaction with the environment. Key parameters are light, heat, oxygen, environmental pollutions like nitrogen oxides and sulphur oxides, and energy rich radiation. This results in aging processes during storage. Ameliorating counter measures are described in Chapter 7.

During operational use, aging is increased by more influencing factors. There are chemical, thermal and mechanical influences, which promote aging. Although aging is aligned to operational disadvantages, it is a calculable and limitable phenomenon concerning its properties and quality characteristics.

There are several groups of plant chemicals, which have to be assessed for aging:

- Lubricants for plant components such as lubricating oil and lubricating grease,
- insulating oil for safety related transformers,
- diesel fuel for emergency power supply,
- refrigerating medium, hydraulic oil,
- other chemicals used in safety related components.

By an aging programme, time dependent changes in the property or quality of the products are assessed and controlled. By identification of changes in time using chemical and physical analyses, countermeasures can be introduced.

In contrary to aging of plant components from mechanical engineering, electrical engineering and control engineering, aging of plant chemicals is much easier to handle, as most of the products are dissipated and replaced by new ones.

8.2 Aging by oxidation and humidity

If mineral oil at increased temperatures comes into contact with oxygen, oxidation products or polymers can be produced. These processes are temperature dependant and change the physical and chemical properties of the products. Therefore, the lubrication capacity in case of lubricating oil, or the isolation efficiency can decrease.

Humidity, or even worse water, changes lubricating efficiency and influences the additives in the oil. Those can be eluted or hydrolysed and transformed into oil-insoluble products, which can precipitate and block small bore holes and other narrow cross sections. By losing the corrosion inhibitors, the lubricant loses its stability against oxidation, what means that he destruction process accelerates. Losing corrosion inhibitors also means that the material within the lubrication system can corrode under formation of solid corrosion products, which can be abrasive and can block narrow cross sections.

Periodic sampling and measurements can trace this aging. Corrective actions are partly or total changing the products or switching the systems to purification facilities.

8.3 Aging by radiation

Examinations about the stability of organics against radiation were made during the first years of commercial use of nuclear energy. But it became clear that in NPP with light water reactors, only a very few lubricated components are in areas with high dose rates in the sense of potential lubricant degradation by radiation. In nearly all cases, conventional lubricants as used in other (fossil) thermal power plants can be used. The situation in gas cooled reactors, high temperature reactors and fast breeder reactors might be a little different in specific locations, but until today, no negative information about operational obstacles has been published.

The following technical expertise is from Rodenbusch and Prokop, who have made their own experiments at a 5 MW pool reactor. Most experiments were made in static conditions.

8.3.1 Impact of radiation on mineral oil

Lubricants consist of a mixture of many organic components, each of them having its own sensitivity or stability against radiation. A big variety of radicals and ions are generated, resulting in numerous radiation products.

In hydrocarbons The -C-C- and -C-H bonds are cracked rather easily generating radicals, which react under formation of hydrogen, short chain hydrocarbons, and bigger radicals, which can undergo several reactions up to polymerisation and cross link reactions.

Aromatic hydrocarbons are more stable against radiation as they have more possibilities to get rid of the energy by internal electron transports. The behaviour of different organics against radiation is shown in Table 8-1.

Table 8-1: Behaviour of organic under radiation [Rodenbusch & Prokop, 1973].

Reaction	Saturated hydrocarbons (G-value)	Unsaturated hydrocarbons (G-value)	Aromatic hydrocarbons (G-value)
Polymerisation	<= 0.1	10 – 10 000	<= 0.05
Cross Linking/ Branching	about 1	6 -14	< 1
Formation of hydrogen	2 – 6	1	0.04 – 0.4
Formation of methane	0.06 – 1	0.1 – 0.4	0.001 – 0.08
Destruction of the material	4 – 9	6 -2 000	<= 1

8.3.1.1 Lubricants on mineral oil basis

Physical properties and lubrication efficiency are changed in different amounts by the influence of radiation. The indications for destruction by radiation are formation of gas, changing the viscosity, deterioration of the oxidation stability, deterioration of the corrosion inhibition, bathochromatic shift, formation of sludge and offensive smell.

Changes of physical data in most cases are only recognized when the radiation dose exceeds 10^6 Gray. A typical change in kinematic viscosity in correlation to radiation dose is shown in Figure 8-1. These are commercial paraffin- and naphthenic-basic oils with viscosities between 30 and 650 cSt at 37.8 °C.

9 Summary – Conclusion (Wilfried Rühle, Hartmut Venz, Francis Nordmann)

For a safe operation of NPP, it is necessary that all components such as pipes, tanks, pumps, motors etc. and spare parts are well documented. Non-documented components must not be used. The same procedure should be valid for chemicals and materials which are necessary for operation and maintenance. No not-licensed products should be in the plant, the warehouse and as possible at the whole site of the plant.

By means of the specific French experience and the more general experience summarized by the Swiss and German approach, valuable hints for establishing plant specific procedures for these products are introduced.

The various aspects to consider with incoming goods are described in details in the document. The overall process is summarized in Table 9-1, referring to each section of the document for the detailed process.

As many of the operational chemicals are hazardous substances, an overview about the legal requirements in the European Union for hazardous substances is presented. For non European operators, their respective legislation has to be followed. In case that there are no regulations in this regard, it might be useful to take the European ones as a guide. The cited IAEA safety Guide should be followed by all operators.

Very important is having a management system for operational chemicals, which deals with the processes for requiring, acquiring, receiving, handling and releasing them as waste. For each of these processes, very helpful flow diagrams are presented.

For many products such as lubricants, cleaning agents, fluids for crack testing, tapes and labels, dye and paint, operational chemicals, IER, chemicals for water treatment, insulating materials, transparency film etc., specifications for quality and allowable impurities are established.

The special status for laboratory chemicals is pointed out. Main aspects here are registration, labelling and expiration management of the chemicals.

Great emphasis is given to the storage of chemicals, especially hazardous ones. This point is very often a big item, when international organisations, like Operational Safety Review Team (OSART) from IAEA or peer review teams from WANO[4], review plant operation. The reason is the risk of unwanted reactions endangering the plant and its personal.

Aging of products during storage should not be underestimated. Regular quality checks are necessary and a schedule for expiring of the usability and the exchange of these chemicals should be available.

A minor problem is aging by use in the plant because of radiation. It could be shown that the dose rates or the radiation doses in areas, where operational chemicals, predominantly lubricants and IER, are used, are normally too low to generate radiation damage during the application time for the products.

[4] World Association of Nuclear Operators (www.wano.org.uk)

Table 9-1: Practical hints for management of incoming and hazardous goods.

Management of incoming and hazardous goods			
	Decisions to make	**Necessary actions**	**Section/ Chapter**
Reasons for program	• Acquire background	• Read basic considerations	2.1 - 2.2 - 2.3
Require chemicals	• Check the necessity of the product	• Coordination between departments	4.1.1
	• Check if alternative products are still in use at the plant	• Check the product list • Follow the minimization order	2.3
Acquire chemicals	• Check the accordance with legislation	• Check chemical cct • Check ordinance on hazardous substances • Check reach • Check GHS • Check IAEA safety guide	3.1 3.2 3.3 3.4 3.5
	• Look for a qualified supplier	• Establish a list of suppliers	4.1.2
	• Make a product specification	• Check Swiss- German approach • Check French approach • Alternative: make your own specification	Chap. 0 2.3 + 2.4
Laboratory chemicals	• Keep in mind the different treatment compared to operational goods	• Check basic principles • Check storage duration • Check labelling • Make the registration	6.1 6.2 0 6.4
Receive chemicals	• Perform an assessment of the goods	• Perform qualitative assessment • Perform quantitative assessment	4.1.3 0
Storing the goods	• Define to which group of chemicals the product belongs • Define the storage place	• Differ between acids, bases, solvents, oxidizers, water-reactive chemicals, pyrophoric chemicals • Light sensitive chemicals, peroxide forming chemicals	7.3.2
Aging management	• Check aging by storage duration	• Define the max. storage duration • Make a schedule for recurrent tests • Define the decision for disposal	8.1 + 8.2
	• Check aging by use	• Make a schedule for product exchange	
	• Check aging by radiation	• Define products influenced by radiation • Make a schedule for product exchange	8.3
Waste treatment	• Find out the waste product group • Collect the waste product separately or product specific	• Look in Chapter 3 because of waste	4.1.5

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