

catalyst handling procedures to minimize exposures

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SUMMARY

This report outlines a generalized approach to reducing worker exposure to solid and liquid catalysts during refinery catalyst handling activities such as reactor loading, unloading and screening.

Many catalyst handling operations have the potential for generating airborne dust, mist or vapour, depending on the nature of the catalyst involved, and due care and attention is necessary to prevent adverse health effects. The report stresses that engineering controls should be adopted as the primary means of minimizing exposures, although it acknowledges that the use of personal protective equipment, such as respirators, goggles and gloves, is also necessary in many catalyst handling activities.

1. INTRODUCTION

Although the health effects associated with exposure to catalysts such as alumina, platinum, silver, cobalt-molybdenum and hydrogen fluoride, vary, the adoption of a general procedure for catalyst handling can assist in ensuring that effective health protection is achieved in the workplace.

With the exception of hydrofluoric, sulphuric and phosphoric acids, the catalysts are usually in the form of granular solids which, when disturbed or otherwise handled, can generate airborne dusts, similarly the liquid catalysts may generate mists and vapours. Both solid and liquid catalysts may, therefore, present opportunities for exposure by inhalation and skin contact and some control of exposure will always be required, regardless of catalyst type. Ideally, engineering controls will reduce the levels at source, but procedural controls and the use of personal protective equipment may also be appropriate depending on the assessment of risk.

2. CATALYST TYPES

A list of the catalyst types typically used in refining processes is shown in **Table 1** and the materials associated with the various catalytic processes in refineries are shown in **Table 2**.

Industrial catalysts may be classified in two basic groups: homogeneous catalysts, where the catalyst is in the same phase (generally in solution) as the reactants, and heterogeneous catalysts, where the catalyst is in a different phase (generally solid) from the reactants (liquids or vapours).

Many modern catalysts used in heterogeneous processes are extremely complex. Most consist of one, two or three principal components often carried on a support material which usually plays no part in the chemical process and is thereby termed "inert". It is usual, however, for other components to be added to modify the performance of the catalyst. These extra components can be "activators" or "promoters" which are added to enhance the rate of particular reactions. They can also be "inhibitors", "dopants" or "partial poisoning agents" which are added to prevent the occurrence of unwanted reactions. The activating or inhibiting action is sometimes achieved by adding a component to the chemical feedstock so that it will interact with the catalyst during the operation of the chemical process.

2.1. FIXED BED CATALYST

The majority of catalysts are utilized in fixed bed reactors, with the feed entering the top of the reactor, spreading across the catalyst bed, and exiting after passing through the bed and exit nozzles. Catalyst particles are cylinder-shaped, ring-shaped, or exhibit other complicated geometries that provide large surface areas for reactions to occur and which do not cause large pressure differentials.

Hydrotreating (combining hydrogen with other molecules for desulphurization), cracking (forming smaller molecules), and general hydrogenation (saturation) are the processes most widely utilising fixed bed catalytic systems. Fixed bed catalysts are also used in steam reformers (deconstructing light hydrocarbons with steam to form hydrogen), ammonia plants, reformers (producing high octane components from paraffins and naphthenes), and aromatics saturation units.

Fixed bed catalysts are typically composed of an alumina or alumina silica support (backbone particle), with metal or metal salts at the particle interstices. The composition of these catalysts ranges from 100% aluminium oxide to 50% nickel or chromium on alumina. Other frequently used fixed bed catalysts contain zinc oxide, cobalt, molybdenum, and silica. Although the metals are located on the surface of particles in order to obtain the best process results, grinding usually does not generate a dust that is different in composition from the bulk particles.

Table 1 Catalysts Employed in Refinery Processes

PROCESS	OPERATION	CATALYST
Light Hydrocarbon Processing		
Polymerization	Produce high octane gasoline or a petrochemical feedstock from gaseous olefins	Usually phosphoric acid dispersed on an inert support
Alkylation	Chemical reaction of low molecular weight paraffin and isoparaffin to form multiple-branched paraffins of high octane rating.	Anhydrous sulphuric or anhydrous hydrofluoric acid
Naphtha Hydrode-sulphurization	Remove sulphur	Non-noble metal catalyst, generally cobalt-molybdenum
Isomerization	Convert straight-chain butane, pentane and hexane into isomers that have higher octane rating	Fixed bed or chlorinated platinum-aluminium oxide. Nickel on silica-alumina
Catalytic Reforming	Convert low octane naphthas into high octane gasoline blending stocks	Fixed bed reactors containing platinum or platinum-rhenium
Middle Distillate Processing		
Chemical Sweetening	Eliminate mercaptans to reduce product odours	Nickel/alumina on activated charcoal
Kerosine and Gas Oil Hydrode-sulphurization	Remove sulphur, saturate any olefins and reduce the aromatic content and gum forming tendency of kerosine and nitrogen and metallic contaminants	Fixed bed reactor containing a non-noble metal normally nickel- or cobalt-molybdenum
Fluid Bed Catalytic Cracking	Convert distillate oils into a wide boiling range material from which catalytic gasoline, heating and gaseous hydrocarbons are obtained	Variety of acid-function catalysts including natural clays, silica-aluminas, and synthetic zeolites in the form of a very fine powder.
Moving Bed Catalytic Cracking	As above	Same type of catalyst as above but in the form of extruded pellets.
Catalytic Hydrocracking	Convert heavy feedstocks into lower boiling, more valuable products	Cobalt-molybdenum or nickel-molybdenum on alumina and/or noble metal eg palladium on silica/alumina
Heavy Hydrocarbon Processing		
Residue Catalytic Cracking	Treatment of heavy oil fraction with heat in presence of a catalyst to give lower molecular wt. products	Normally nickel/molybdenum
Residue Hydrocracking	Treatment of heavy oil fraction, with high pressure hydrogen to give lower molecular wt. products	Metal sulphides on amorphous silica-alumina
Residual Oil Hydrode-sulphurization	Reduce the sulphur and metal contents of atmospheric tower residues	Active components typically chromium, molybdenum, iron, cobalt or nickel
Lube Oil Hydrotreating Hydrocracking	Treatment of the oil with hydrogen to improve product quality	Cobalt- or nickel- molybdenum
Catalytic Dewaxing	Removal of paraffin wax from lubricating oils	Zeolites

2.2. FLUID BED CATALYST

A major commercial fluid bed process that currently uses catalyst is the Fluid Catalytic Cracking (FCC) Unit. This unit utilises a synthetic zeolite catalyst to crack heavy feeds and produce, primarily, gasoline and heating oil with a minimum of coke and gas formation. Zeolite catalyst is a synthetic mixture of hydrated alumina and calcium silicate (some as molecular sieve) with a trace of rare earths. The catalyst is in powder form and circulates by means of pressure differences and gravity between the reactor and the regenerator. The primary reactions take place just after feed is introduced into a line leading to the reactor. Since the catalyst is fluidized, it has to be separated from reaction gases and recycled. However, fines are generated in the recycling process and some escape from the system; hence make-up catalyst has to be added continuously.

In the last ten years, metal additives have been added to FCC catalyst to diminish the catalyst poisoning effects of nickel and vanadium in the feed material. However, the additives are at such small concentrations that they do not contribute significantly to the overall toxicity of the catalyst.

2.3. LIQUID BED CATALYST

Liquid bed systems are those processes in which the catalyst and liquid reactants cannot be separated physically by simple exit nozzles. Liquid bed reactors include homogeneous reactors where the catalyst and the reactants are in the same (liquid) phase, and slurry reactors where the catalyst is removed from the products by filtering or centrifuge. The use of liquid catalysts in downstream operations is primarily in the conversion of isobutane and butylenes to iso-octane using hydrofluoric and sulphuric acids (alkylation). Liquid bed reactors are of special health interest because of the increased concern for skin/eye contact with these strong acids and the additional equipment required for loading and unloading liquid catalyst.

2.4. SPENT CATALYST

In industrial use, catalysts lose their effectiveness due to overheating and poisoning. Substances which affect catalytic efficiency adversely include metals entrained in the feedstocks; oxygen, nitrogen or sulphur compounds; and coke formed from polynuclear aromatic compounds. As catalysts lose activity - or if the porosity of the catalyst bed becomes clogged by coke - the catalyst has to be replaced or regenerated.

Although few additives are present at high enough concentrations to alter the overall toxicological properties of catalysts, some toxicologically-important substances may be formed during catalytic reactions. For example, metal carbonyls, particularly nickel carbonyl, are formed by reaction of carbon monoxide with nickel-containing catalyst at low temperatures and high pressures, whereas nickel subsulphide, a suspected carcinogen, is formed in reduced nickel containing catalyst, and may be found in minute quantities (ppm) in some spent catalyst.

In addition to the chemical hazards a number of unique physical hazards need to be considered when working with pyrophoric catalysts, and these are referred to in Section 6.2.

Table 2: Materials Associated With Catalytic Processes

MATERIAL	PRINCIPAL USES OR SOURCES OF EMISSION
Alumina (aluminium oxide)	Catalyst support, catalyst (sulphur recovery)
Aluminium chloride	Isomerization
Amines, aliphatic (e.g. methylamine) and alkanol amines (e.g. monoethanol-amine)	Hydrodesulphurization, and gas absorbents
Amines, aromatic (e.g. anisidines and phenylenediamines)	Catalytic cracking, residual processing
Antimony trichloride	Inhibitor (isomerization)
Carbon monoxide	Catalyst regeneration (catalytic cracking)
Chlorine	Rejuvenation of platinum catalyst
Clays (e.g. bentonite)	Catalyst supports
Cobalt and cobalt compounds (cobalt carbonyl, cobalt molybdate, cobalt oxides, cobalt phthalocyanine sulphonate)	Hydrocracking, hydrotreating, merox and similar sweetening processes
Copper and copper compounds (e.g. copper chloride, copper alloys)	Desulphurization, sweetening operations,
Earth, diatomaceous (amorphous silica)	Catalyst support
Hydrocarbons, chlorinated	Rejuvenation of catalyst (catalytic reforming)
Hydrogen chloride	Isomerization
Hydrogen fluoride (hydro-fluoric acid)	Alkylation
Hypochlorites	Chemical sweetening (oxidising agent)
Iron and iron compounds	Hydrocracking
Molybdenum and molybdenum compounds	Desulphurization, hydrocracking, hydrotreating
Nickel and nickel compounds (e.g. nickel sulphides, nickel carbonyl, nickel oxide)	Hydrotreating, hydrocracking,
Palladium	Hydrotreatment, hydrocracking
Phenol	Catalytic cracking, desulphurization
Phosgene	Catalyst rejuvenation by chlorination (catalytic reforming)
Phosphoric acid	Polymerization
Platinum	Catalytic reforming, isomerization, hydrotreating
Rhenium	Catalytic reforming
Silica, crystalline	Catalytic cracking
Silver	Catalytic oxidation (ethylene to ethylene oxide)
Sodium hydroxide	Caustic wash of acid catalysts or acid-treated streams
Sulphuric acid	Alkylation, polymerization
Tungsten sulphide	Hydrocracking
Vanadium metal and compounds	Catalytic oxidation
Zeolite (synthetic)	Fluid catalytic cracking, hydrocracking
Zinc oxide	Catalytic oxidation

3. HEALTH PROTECTION

This section briefly outlines the main sources of exposure to catalysts in refinery processes and summarizes the adverse effects associated with significant exposures to some of the catalysts utilised. It also addresses the key practical aspects of the assessment and control of the health risks, activities which are essential features in effective health protection programmes.

3.1. SOURCES OF EXPOSURE

The main opportunities for exposure arise during the addition of fresh catalyst, the removal and drumming of spent catalyst, the screening of used catalyst and the removal of elbows, thermocouples, etc. from reactor vessels.

3.2. HEALTH EFFECTS

The health effects arising from exposure to catalysts depend on their form composition and the extent of exposure that may occur. The effects include skin irritation and sensitisation (some metal-based catalysts), fibrogenicity (naturally occurring zeolites) and corrosion (acids).

3.2.1 Metal/Metal Salt Based Catalysts

The principal effects associated with some metal/metal salt based catalysts are summarized in **Table 3**. These range from mild irritation to the skin and eyes, to possible carcinogenicity.

3.2.2 Zeolite Catalysts

The main interest from a health viewpoint is the possible fibrogenic nature of the naturally occurring material. The degree of fibrogenicity is dependent on the type of zeolite involved, although synthetic zeolites are normally non-fibrogenic in nature.

3.2.3 Acid Catalysts

Hydrofluoric acid (HF) and sulphuric acid are both strongly corrosive. HF liquid or vapour, in contact with any part of the body, causes serious and extremely painful burns, if not treated properly. On the other hand, contact with a dilute solution of HF may not result in pain or visible effects until hours after skin exposure has occurred.

Table 3: Primary health effects associated with some metal/metal salt based catalysts

METAL	FORM	HEALTH HAZARDS
Cobalt	oxide	Dust can be mildly irritating to eyes, skin & mucous membranes.
Molybdenum	oxide	Dust can be mildly irritating to eyes, skin & mucous membranes.
Nickel	oxide	Dust can be mildly irritating to eyes, skin & mucous membranes. Nickel is a skin sensitiser and nickel oxide and sulphide are carcinogenic.
Iron	oxide	Long term exposure to dust can have effects on lungs as revealed by X-ray changes.
Chromium	chromate	Dermatitis has been reported in workers handling trivalent chromium compounds.
Silver	metal	Silver compounds can result in argyria, a permanent blue-grey discolouration of the skin, mucous membranes or eyes. This is a cosmetic effect and does not interfere with the health of the individual. Inhalation of dusts can cause irritation & inflammation of the respiratory tract.
Platinum	metal	Dust, aerosols or mists from platinum salts are sensitisers of mucous membranes, skin & respiratory tract.
Extruded alumina		Dust can be mildly irritating to the skin and mucous membranes.

3.3. ASSESSMENT OF HEALTH RISKS

The foundation to ensuring effective health protection during the handling of catalysts is a formal assessment of the health risks associated with all the relevant operational and maintenance tasks. This should be carried out in accordance with the requirements of existing Directives on Health and Safety at Work. From a practical point of view, this initially involves:

- identifying all relevant tasks
- establishing an inventory of the catalysts handled
- acquiring health and safety information relating to the catalysts
- identifying other hazards (e.g. ergonomic factors, pyrophoric properties, noise and oxygen deficiency) associated with the handling of the catalysts

Then, from inquiry, task observation and, where relevant, exposure monitoring (see below), the actual risks can be evaluated by a suitably competent person, taking full account of any existing control measures, and conclusions drawn as to the adequacy of the prevailing procedures. The assessment should identify any additional measures needed to ensure the adequate control of health risks.

3.3.1. Exposure Monitoring

Sometimes, as part of the risk assessment, it is helpful to conduct workplace monitoring to ascertain the typical occupational exposures to catalyst dust, mist or vapour for both routine and non-routine activities. It may also be deemed appropriate, in some circumstances, to introduce a programme of regular monitoring subsequent to the assessment to ensure that the acceptable conditions found during the initial assessment, or established subsequently, are maintained. For both the initial and routine monitoring it is important that:

- the sampling strategy should be sufficiently extensive to allow an adequate evaluation of exposures to hazardous substances covering the whole range of circumstances encountered at work;
- the results should include information on the sampling and analytical methods adopted. Only validated analytical methods should be used and, if possible, the analytical laboratory should participate in an appropriate quality assurance programme.

It is suggested that the occupational exposure limits given in **Table 4** should be used when evaluating the results of exposure measurements during catalyst handling, except where relevant national occupational exposure criteria have been established.

3.4. CONTROL OF HEALTH RISKS

Where the assessment indicates that it is necessary, additional control measures should be introduced to ensure adequate protection against the identified health risks. Where reasonably practicable this should be achieved by the introduction of engineering measures that lead to improved containment. The use of personal protective equipment, which protects the wearer from the work environment, should be adopted only after alternative means of attenuating exposure have been considered and found to be either impracticable or requiring additional measures (e.g. to minimize the risk in the event of primary control failure) from the work environment, should be regarded as a last resort, but is necessary where the other measures are not feasible, or not regarded as entirely sufficient on their own.

Table 4: ACGIH 1994-1995 Threshold Limit Values for Chemical Substances

Substance	Adopted values 8 Hour Time Weighted Average mg/m ³	Intended Changes Weighted Average mg/m ³	Adopted 15 Minute Shorter Exposure Limits mg/m ³
Aluminium oxide, as Al	10	-	-
Antimony and compounds as Sb	0.5	-	-
Chromium, metal and inorganic compounds as Cr			
Metal and Cr III compounds	0.5, A4	-	-
Water-soluble Cr VI compounds	0.05, A1	-	-
Insoluble Cr VI compounds	0.01, A1	-	-
Cobalt as Co			
Elemental and inorganic compounds	0.02, A3	-	-
Cobalt carbonyl, as Co	0.1	-	-
Copper			
Fume	0.2	-	-
Dusts & mists, as Cu	1	-	-
Molybdenum, as Mo			
Soluble compounds	5	-	-
Insoluble compounds	10	-	-
Nickel			
Metal	(1)	0.05, A1	-
Insoluble compounds as Ni	(1)	0.05, A1	-
Soluble compounds, as Ni	(0.1)	0.05, A1	-
Nuisance particulates - particulates			
Not otherwise Classified (PNOC)	10	-	-
Platinum			
Metal	1	-	-
Soluble salts, as Pt	0.002	-	-
Silica-Amorphous			
Diatomaceous earth (uncalcined)	10	-	-
Silver			
Metal	0.1	-	-
Soluble compounds, as Ag	0.01	-	-
Tin			
Metal	2	-	-
Oxide & inorganic compounds, except SnH ₄ , as Sn	2	-	-
Tungsten, as W			
Insoluble compounds	5	-	10
Soluble compounds	1	-	3
Vanadium, As V ₂ O ₅			
Respirable dust and fume	0.05	-	-
Zinc oxide			
Fume	5	-	10
Dust	10	-	-

A1: Confirmed human carcinogen
A3: Animal carcinogen
A4: Not classifiable as a human carcinogen

It is emphasised that the most practicable and cost-effective opportunity to address the control of health risks is at the design stage of any new catalyst operation, or where a catalyst activity is being modified in some way.

3.4.1. Engineering Controls

The starting point for the control of exposure to catalyst dust, mist or vapour, is best achieved by the introduction of engineering measures, such as enclosures, local exhaust ventilation or wet scrubbers, that lead to improved containment. The emphasis should always be directed to maximum containment - and this is particularly important with hydrogen fluoride.

To prevent the escape of dust during catalyst unloading operations, for example, the dumping chute - and associated drum or container - should be enclosed using a close weave cloth or metal sleeve. If the sleeve is maintained under a negative pressure, the exhausted air should be filtered using high efficiency filters before being released to the environment. The extract fan should be located as close as possible to the filter, in order to minimize the amount of ducting under positive pressure. Filtered dust and fines should be collected in a drum or other suitable container for reclamation.

Wet collection systems can be used to minimize dust emission but disposal of the slurry can present a problem. To prevent the escape of catalyst dust during screening operations, the screening equipment should be operated under a negative pressure and a close weave cloth sleeve utilized to enclose the discharge chute and associated drum. The sleeve should be maintained under negative pressure and the exhausted air filtered using high efficiency filters.

3.4.2. Administrative Controls

Work involving the handling of catalyst is normally subject to a 'permit-to-work' system that specifies the necessary control measures. These should be applied rigorously.

The catalyst handling area is normally screened or roped off to exclude entry by unauthorized personnel. The extent of the designated area should take account of the wind direction and, in addition, an allowance made for the access of forklift vehicles and dust extraction equipment, where these are necessary.

3.4.3. Personal Protective Equipment

Where adequate control cannot be achieved by other methods, personnel working directly with catalyst (eg loading, unloading, screening, sealing drums and cleaning up spills) should wear protective overalls, goggles, gloves and boots as required. It is important that protective clothing is selected carefully, worn properly and maintained as specified. Clean protective clothing should be provided not only at the beginning of each shift but also whenever protective suits are torn or otherwise damaged. Contaminated protective clothing should be discarded into a properly labelled bin for laundering or disposal as chemical waste.

Respiratory Protection

Where indicated by the assessment of risk or if required by local regulations, personnel handling solid catalyst during loading or unloading operations (screening, sealing drums, cleaning up spills, etc.) should wear approved dust filter respirators or full-face air supplied breathing apparatus, depending on the risks. All

maintenance personnel directly involved in the removal of bottom elbows from the reactor and installation of a loading chute, or engaged in other activities producing dust should also use suitable respiratory protection, as should those personnel entering the screened or roped-off exclusion area during catalyst loading and unloading, screening activities, sealing drums and removing drums.

It is important that all personnel required to wear respiratory protective equipment during catalyst loading or unloading operations, should conform to a 'no facial hair' requirement to assist in ensuring that a proper seal is achieved between the respirator and face. Alternatively it is suggested that an 'air-stream' type helmet might be utilised if only low level protection is needed.

Personnel entering a reactor to remove baskets prior to catalyst unloading should wear full-body protective clothing, gloves, boots, lifeline in addition to full-face air-supplied respirators. It is preferable to use positive pressure rather than demand only systems. "Air stream" type helmets should not be used in these circumstances as they may not provide adequate protection.

Personnel acting in a safety observer capacity, in accordance with confined space entry procedures, should also wear the approved protective clothing and have air-supplied equipment readily available for use in an emergency. The safety observer should also have suitable communication equipment to obtain assistance should an emergency arise.

Where catalyst is handled off-site, the designated area should be restricted to essential personnel. The same protective measures should be adopted as for on-site catalyst handling. Air-supplied respiratory protection should be worn if spent catalyst stocks start to smoulder.

3.4.4. Personal Hygiene

To prevent the ingestion of catalyst dust, no eating, drinking or smoking should be permitted in the catalyst handling area. Personnel working with catalyst should follow good personal hygiene practices by washing their hands and face with soap and water before and after working with catalyst material, as well as prior to eating, smoking or using toilet facilities.

Protective, outer work clothes should be removed at the end of the shift or more frequently if they become heavily contaminated with catalyst dust. It is preferable to use disposable overalls when handling catalysts containing metallic sensitisers, such as nickel and platinum, or where heavy contamination of clothing occurs. Contaminated clothing and other protective equipment should not be re-worn until they have been thoroughly laundered or decontaminated and should not be taken home from the workplace. Disposable work clothes should be removed before leaving the work area and placed in a suitable container for disposal. Showers are recommended before changing into home clothing which ideally should be kept in a locker separate from work clothes.

3.4.5. Maintenance, Examination and Testing of Control Measures

The 'design-specification' performance of the engineering controls and many types of personal protective equipment will not be achieved unless they are examined, tested and maintained on a regular basis by suitably qualified persons. Detailed records of such examinations should be kept in a suitable format for at least 5 years.

4. OTHER FEATURES

4.1. INSTRUCTION AND TRAINING

A programme providing information and instruction on all aspects of catalyst handling should be available to those directly involved and should be in accordance with legislative and company requirements. In many cases this may well form part of a wider programme of instruction and training regarding work with substances hazardous to health.

Employees should be regularly trained in the correct use of appropriate control measures, be aware of their duties to report any defects and know the control procedures to apply in the event of an emergency.

Effective health and safety protection in handling HF, in particular, is dependent on the effectiveness of the instruction and training about the hazards and risks, the safe practices to be adopted, the use of appropriate protective equipment and provision of competent supervision. In the case of HF, training should be given on the specific procedures for first aid or emergency medical treatment.

4.2. RESOURCES

Sufficient manpower should be dedicated to all health protection activities, including those involving catalysts, and adequate training provided to ensure that the various aspects of such activities may be performed competently. Sufficient health and safety information should be available to line managers, employees and health and safety practitioners, particularly legislation standards and company guidelines, and this information should be up to date.

4.3. RECORDS

Where applicable, suitable records should be retained on all aspects of the health protection programme relating to 'catalyst handling', including the results of health risk assessments/exposure measurements, the maintenance, examination and testing of control measures, such as local extract ventilation and personal protective equipment, and the instruction and training of employees about the health risks associated with working with catalysts and the precautionary measures to be followed.

The records, accompanied by an interpretation of the data, should be stored in accordance with national law and practice, retained in an easily retrievable form and be available to employees. Furthermore, where appropriate, they should include process information, such as operation, plant status, procedures used. With the exception of the maintenance, examination and testing of control measures (see **Section 3.4.5**), the records of this nature should be kept for a minimum of 40 years.

5. LABELLING AND TRANSPORT

Labelling of spent catalyst must conform with appropriate national requirements for the supply and/or conveyance of such materials. In particular the requirements of the Hazardous Waste Directive should be met. Drums of spent catalyst, for example, should be properly labelled with an appropriate warning statement, such as:

<p>CAUTION Spent Catalyst (Specify Type) Avoid Breathing Dust or Contact With Skin</p>
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taking full account of the chemical species present. For example if the spent catalyst contains sulphides of nickel it will have different toxicological properties to the native nickel oxides catalyst, whilst if the spent catalyst is pyrophoric, this should be indicated clearly on the label.

6. EMERGENCY PROCEDURES

6.1. CLEAN-UP

All spilled catalyst powder should be promptly cleaned up in such a way that the emission of airborne dust is minimised. Appropriate techniques include vacuuming, wet mopping, the use of sweeping compounds, and shovelling. Under no circumstances should dry sweeping be carried out.

The entire catalyst handling area should be washed down or vacuumed at the completion of a catalyst handling operation. However, neither spilt catalyst nor settled catalyst dust should be washed into any public water system. All spilt or used catalyst should be placed in containers, sealed promptly and labelled prior to metal recovery or authorized disposal.

6.2. PYROPHORIC CATALYSTS (PLATINUM, COBALT-MOLYBDENUM, NICKEL-MOLYBDENUM)

In addition to the chemical hazards associated with catalyst material, a number of unique physical hazards need to be taken into account when working with a pyrophoric catalyst. Particular concern relates to any need to enter a nitrogen-purged (inerted) reactor containing a pyrophoric catalyst, an activity that should be precluded as far as possible. However, where entry is necessary the following procedures and precautionary measures should be implemented:

- Whilst monitoring in relation to the lower explosive limit (LEL) is optional, the oxygen content should be continuously checked during activities requiring entry into a reactor, in order to prevent a build-up of oxygen. The vessel should be vacated and entry prohibited if the oxygen concentration exceeds 2%. One source of oxygen contamination within the reactor is exhaled air from the air supplied respirator.

NB If a reactor is inerted with nitrogen, a conventional explosimeter is not suitable for monitoring (LEL).

- All drums used for spent pyrophoric catalyst should be filled under a nitrogen blanket. In addition, sand or the appropriate fire extinguishant should be available to extinguish any smouldering catalyst. When shipping pyrophoric catalyst solid CO₂ can be placed in the bottom of the drum to generate a CO₂ blanket, as an alternative to having a nitrogen blanket.
- All operational measures normally applicable to entry into non-life supporting atmospheres must be followed, such as maintaining a support person close to the point of vessel entry in order to keep a watch on those personnel working in such atmospheres.

6.3. LIQUID CATALYSTS (HYDROFLUORIC AND SULPHURIC ACIDS)

Readily accessible and clearly identified, rapid action safety showers and eye wash fountains should be installed in all areas where HF and H₂SO₄ are handled. The safety showers should have deluge type heads and preferably activated by simply standing on a plate that is attached to the activating valve. The shower should have a flow rate of 225-360 litres/minute.

In the case of HF, decontamination kits containing calcium gluconate gel should be immediately available for use should skin contact occur and all persons at risk should be given instructions in first-aid treatment.

7. WASTE DISPOSAL

Spent catalysts can present a risk not only to the health of workers but also to the environment, depending on their physical and chemical characteristics. Hence, the handling of such catalysts, whether for disposal or regeneration, requires careful consideration. The main factors that have a bearing on the method of disposal are toxicity (to man and to the environment), bioavailability, biodegradation, bioaccumulation and partitioning.

The options for disposal of a catalyst are limited due to the stability and persistence of the constituents, except where contamination with organic material is present. The most common method is landfill, but this requires an assessment of the potential for leaching into, and contamination of, adjacent strata and watercourses. In all cases of disposal, the emphasis is on long-term assurance that any foreseeable risks to the public and to the environment are negligible.

It is emphasised that the generator of catalyst waste retains the responsibility for the integrity of the disposal method.

8. REFERENCES

This document is largely based on individual company guidelines and on the following publications:

1. Gentry, S.J. et al (1983) Catalysts. In: Encyclopaedia of Occupational Health and Safety. Vol 1, 421-426. Geneva: International Labour Organization
2. Bird, M.G.(1993) Catalysts - their toxicity and potential hazard to health. In: Handbook of Occupational Hygiene, (Instalment 41) Section 8.2, Croner Publishing p 8.2-01/19
3. Kirk-Othmer(ed) (1985) Concise Encyclopaedia of Chemical Technology. New York: Wiley-Interscience
4. API (1992) Recommended Practice No. 751 Safe operation of hydrofluoric acid alkylation units. Washington DC: American Petroleum Institute

APPENDIX I**PERSONAL PROTECTIVE EQUIPMENT TO BE USED WHEN WORKING WITH HYDROGEN FLUORIDE (HF)**

For work with HF, the following personal protective equipment is advocated:

- Eye/face protection: chemical goggles and a full face shield.
- Respiratory protection: selected from
 - Air filter respirators fitted with the appropriate filter canister, although it should be noted that these should not be used in oxygen deficient atmospheres;
 - Air-line supplied full face-piece respirators;
 - Self-contained full face-piece respirators.
- Protective clothing: ranges from acid resistant work clothes to a full air-supplied chemical protection suit. Neoprene is considered to provide effective protection. The American Petroleum Institute (API) provides advice on the protection required for different levels of risk, ranging from Class A (minimum protection) to Class D (maximum protection).

