CRITERION
CATALYSTS & TECHNOLOGIES

TECHNICAL BULLETIN:

Safe Handling of CRITERION* Hydrotreating Catalysts

Hydrotreating catalysts should be handled with caution. These catalysts contain oxides of nickel, cobalt, molybdenum, tungsten, or phosphorous on an alumina or alumina-silica support. The typical composition ranges of these components are:

NiO	0-13%
CoO	0-6%
MoO3	0-30%
WO3	0-30%
P2O5	0-10%
Al2O3	40-95%
SiO2	0 - 45%

HEALTH HAZARDS

Potential carcinogenicity of nickel and cobalt compounds
In nickel smelting operations where high dust levels were present, several studies have found that the workers were exposed to an excessive risk of nasal and lung cancer. Nickel sulphides and oxide were constituents of this dust. Further, lung cancer has been produced experimentally in animals inhaling nickel subsulphide. Some evidence indicates that the cause of this excess incidence of respiratory tract cancer may be confined to nickel subsulphide. However, until more conclusive information is available, all inorganic nickel-containing compounds should be considered to be potentially carcinogenic agents.

Occupational exposure to cobalt-containing dust has also been associated with the development of different pulmonary diseases and lung cancer. These diseases have been mostly confined to workers from the hard metal industry (cobalt-tungsten carbide composite), while workers exposed to cobalt alone do not seem to exhibit this excess of lung cancers.

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Several references listed at the end of this document provide further details.

Other health effects
Nickel and cobalt compounds produce an allergic skin reaction in sensitive individuals. Tests in laboratory animals have not supported the notion that hydrotreating catalysts are sensitisers. Prolonged handling of these metal oxides could develop into a chronic dermatitis. Oxides of all these metals are irritating to the eyes and mucous membranes of the respiratory tract. Other effects are not likely under the conditions of expected handling and use.

Fire and toxicity hazards of used catalyst
As purchased from CRITERION, hydrotreating catalysts are not flammable and require no special precautions against fire. However, during use carbon is formed and deposited on the catalyst, and the transition metals are converted to a chemically reactive "sulphided" state. Nickel subsulphide may be formed during catalyst use. If spent catalyst is warm and contacts oxygen, the ensuing reaction may generate enough heat to ignite carbon deposited on the catalyst. It is possible that this process also might create nickel carbonyl, which has US Occupational Safety and Heath Administration (OSHA) permissible exposure limit of 1 ppb.

Overexposure
In case of skin contact, wash thoroughly with soap and water. In case of eye irritation, flush eyes with water for at least 15 minutes. If irritation persists, get medical attention.

GENERAL HANDLING OF HYDROTREATING CATALYSTS

The following procedures apply to both fresh and used catalyst and are directed at minimising the possibility of dust inhalation and skin contact.

Ventilation and respiratory protection
The following OSHA standards for possible air contaminants pertain to catalyst components:

Substance	mg/m^3 (1)
Nickel	
(metal, soluble and insoluble compounds, as Ni)	1
Cobalt (metal, fume and dust), as Co)	0.1
Molybdenum (soluble compounds)	5
(insoluble compounds, total dust)	15
Alumina (total dust)	15
Alumina (respirable fraction)	5
Silica, amorphous	20 mppcf

(1) Based on an 8-hour time-weighted average exposure

To ensure compliance with these safety standards, catalysts should be handled in an area which is enclosed and/or well ventilated to minimise contamination of the surrounding atmosphere. Where this is impossible, and exposure in excess of a standard is likely, respiratory protective equipment should be worn. When handling fresh catalyst, a US National Institute for Occupational Safety and Health (NIOSH)-approved air-purifying respirator containing a cartridge for dusts, mists, and fume removal should be selected. The fire hazard and possibility of generating nickel carbonyl preclude use of this type of respirator when handling used catalyst. Special precautions to be used when working with used material are discussed below.

Personal hygiene
To minimise skin contact, gloves, apron, and goggles should be worn. If dust levels exceed an OSHA standard, the use of a full-face respirator and full-body protective clothing is recommended. Employees should vacuum their work clothing and shoes prior to leaving the work area and should wash hands and face prior to using the toilet, eating, drinking, or smoking. Food, beverages, candy and tobacco products should not be carried while handling these catalysts. Work clothing should be removed at the end of a shift or sooner if contaminated. Showering before changing into street clothes is recommended.

Housekeeping and spill cleanup
To minimise dust generation, the work area should be vacuumed after handling of catalyst is completed. Likewise, spills should be cleaned up by vacuuming or other means which do not generate dust. Work or spill areas should not be cleaned by dry sweeping or by hosing which could carry the contaminants into a public water system.

Reactor entry
If workers must enter the reactor to aid in loading, unloading or cleaning up residual used catalyst, confined space entry procedures should include the use of full-body protective clothing and a self-contained breathing apparatus or supplied air respirator, which maintains a positive pressure within a full-face mask.

PROCEDURES SPECIFIC FOR SPENT CATALYST

Reactor unloading
After cutting out feedstock, the catalyst should be stripped with hydrogen recycle gas to remove hydrocarbons and some of the sulphur compounds. The amount of stripping required depends upon the feedstock being treated. Continue to strip until no more oil accumulates in the product separator. The reactor temperature should be in the range of 315°-370°C (600°F) during stripping.

For heavy gas oil and lube hydrotreating operations, it is preferable to strip the catalyst with a light liquid stock (such as naphtha) prior to hydrogen stripping.

When a liquid wash is used, the reactor temperature must be reduced to ensure that the wash material is in the liquid phase. The liquid wash should be maintained for 4-8 hours. The colour of the wash effluent should be used to dictate when to stop. Hydrogen stripping should then be provided until no more liquid accumulates in the product separator.

Safe unloading procedures dictate that the catalyst bed be cooled to below 65EC (150°F) by recirculating nitrogen (inert gas) prior to unloading. The inert gas should have replaced the hydrogen recycle gas in order to cool down the system in an oxygen-free atmosphere.

Once cooled, the used catalyst may be emptied into drums for later shipment to a regenerator or a disposal site. If the catalyst is highly pyrophoric (containing iron sulphide, etc.), the catalyst should be dumped into drums containing an internal liner for shipment. The drum and liner should first be filled with inert gas, which is then displaced by the catalyst. The liner should be tied off and a small chunk of dry ice placed inside the drum before sealing. These precautions should protect against catalyst autoignition.

Because of high levels of dust generated during unloading and the possibility of generation of gases against which a cartridge-type respirator is not effective, special protective equipment should be worn during this process. This includes use of a self-contained breathing apparatus or supplied air respirator (which maintains a positive pressure within a full-face mask) and full-body protective clothing.

Disposal

When spent catalyst is unloaded for disposal, follow the hydrogen stripping and drumming procedures outlined above. If it is necessary to dump the catalyst at a temperature higher than 65°C (150 °F), catalyst should be unloaded into drums or pans containing water. All spent catalyst should be loaded into drums for transportation and ultimate disposal at an approved disposal site. Any displaced quench water should be collected and treated to remove residual catalyst metals.

TRANSPORTATION

U.S. Department of Transportation (DOT) regulations or equivalent national or international transportation regulations must be followed when shipping new or used catalyst to customers, or when shipping spent catalysts to a merchant regenerator or a disposal site.

Fresh and regenerated hydrotreating catalysts are usually non-hazardous and non-restricted materials that do not required a UN identification number for shipping. However, shippers should check local, state, national or international regulations to ensure that these are complied with.

Fresh and regenerated catalysts are shipped in supersacks, drums, or flowbins. Non-self-heating and non-pyrophoric spent catalysts can be transported in drums, supersacks, flowbins, roll-off bins, or dumptrucks. Self-heating and pyrophoric spent catalysts are typically shipped in steel drums, flowbins, or rented containers. The latter can also be shipped in special air-tight roll-off boxes which meet DOT requirements.

In all cases, the shipper must determine whether the spent catalysts exhibit one or more hazardous characteristics such as flammability, spontaneous combustion, acute or delayed toxicity, or corrosivity, and ensure that appropriate regulatory requirements are met. These include proper labelling and warnings, use of permitted carriers, waste manifesting, or approval for transfrontier movements of hazardous waste, where applicable. Example of possible hazards and warning statements are given below:

Warning: Flammable Solid
Danger! Contains nickel or nickel compounds. Observe OSHA (or local health and safety) limits. Minimise dust inhalation and skin contact. Potential carcinogen.
Danger! Contains cobalt or cobalt compounds. Observe OSHA (or local health and safety) limits. Minimise dust inhalation and skin contact. Potential carcinogen.

References

Code of Federal Regulations, Title 49, Parts 100 - 199. Transportation.

Agency for Toxic Substances and Disease Registry: Toxicological Profile for Nickel, 1993.

American Conference of Governmental Industrial Hygienists. Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices for 1995-1996.

Who, IARC Monograph on the Evaluation of Carcinogenic Risks to Humans. 1990, 49, Chromium, Nickel and Welding.

Who, IARC Monograph on the Evaluation of Carcinogenic Risks to Humans. 1991, 52, Cobalt and Cobalt Compounds, 363-472.

Lison, Dominique (1996) Human Toxicity of Cobalt-Containing Dust and Experimental Studies on the Mechanism of Interstitial Lung Disease (Hard Metal Disease), Critical Reviews in Toxicology, 26(6), 585-616.

ADDITIONAL INFORMATION

All catalyst information supplied by CRITERION is considered accurate but is furnished with the express understanding that the customer receiving such information shall make its own assessments to determine suitability of such information for customer's particular purpose. All purchases of catalyst from CRITERION are subject to CRITERION's standard terms and conditions of sale (including CRITERION's product warranties) set forth in a sales proposal, sales contract, order acknowledgement, and/or bill of lading.

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