Environmental, Health, and Safety Guidelines
LARGE VOLUME INORGANIC COMPOUNDS MANUFACTURING AND COAL TAR DISTILLATION

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Environmental, Health and Safety Guidelines for Large Volume Inorganic Compounds Manufacturing and Coal Tar Distillation

Introduction

The Environmental, Health, and Safety (EHS) Guidelines are technical reference documents with general and industry-specific examples of Good International Industry Practice (GIIP)[1]. When one or more members of the World Bank Group are involved in a project, these EHS Guidelines are applied as required by their respective policies and standards. These industry sector EHS guidelines are designed to be used together with the **General EHS Guidelines** document, which provides guidance to users on common EHS issues potentially applicable to all industry sectors. For complex projects, use of multiple industry-sector guidelines may be necessary. A complete list of industry-sector guidelines can be found at: www.ifc.org/ifcext/enviro.nsf/Content/EnvironmentalGuidelines

The EHS Guidelines contain the performance levels and measures that are generally considered to be achievable in new facilities by existing technology at reasonable costs. Application of the EHS Guidelines to existing facilities may involve the establishment of site-specific targets, with an appropriate timetable for achieving them.

The applicability of the EHS Guidelines should be tailored to the hazards and risks established for each project on the basis of

the results of an environmental assessment in which site-specific variables, such as host country context, assimilative capacity of the environment, and other project factors, are taken into account. The applicability of specific technical recommendations should be based on the professional opinion of qualified and experienced persons. When host country regulations differ from the levels and measures presented in the EHS Guidelines, projects are expected to achieve whichever is more stringent. If less stringent levels or measures than those provided in these EHS Guidelines are appropriate, in view of specific project circumstances, a full and detailed justification for any proposed alternatives is needed as part of the site-specific environmental assessment. This justification should demonstrate that the choice for any alternate performance levels is protective of human health and the environment.

Applicability

This EHS Guideline includes information relevant to chemical manufacturing projects and facilities, and covers the production of large volume inorganic compounds (LVIC), including ammonia, acids (nitric, hydrochloric, sulfuric, hydrofluoric, phosphoric acid), chlor-alkali (e.g. chlorine, caustic soda, soda ash, etc.), carbon black, and coal tar distillation (naphthalene, phenanthrene, anthracene). This document is organized according to the following sections:

Section 1.0 — Industry-Specific Impacts and Management
Section 2.0 — Performance Indicators and Monitoring
Section 3.0 — References and Additional Sources
Annex A   — General Description of Industry Activities

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[1] Defined as the exercise of professional skill, diligence, prudence and foresight that would be reasonably expected from skilled and experienced professionals engaged in the same type of undertaking under the same or similar circumstances globally. The circumstances that skilled and experienced professionals may find when evaluating the range of pollution prevention and control techniques available to a project may include, but are not limited to, varying levels of environmental degradation and environmental assimilative capacity as well as varying levels of financial and technical feasibility.

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1.0   Industry-Specific Impacts and Management

The following section provides a summary of EHS issues associated with facilities manufacturing large volume inorganic compounds (LVIC) and for coal tar distillation, which occur during the operational phase, along with recommendations for their management.

Recommendations for the management of EHS impacts common to most large industrial facilities during the construction and decommissioning phases are provided in the **General EHS Guidelines**.

1.1   Environmental

Typical environmental issues associated with LVIC manufacturing include the following:

- Air emissions
- Liquid effluents
- Generation of solid waste
- Hazardous materials management
- Noise
- Odors
- Decommissioning

Air Emissions

The manufacture and use of inorganic chemicals and chemical products typically generate s large volume of emissions; however, current technology allows for closed system operations, thus significantly reducing emission releases to the environment.

Emission sources from chemical processes include process tail gases, heaters and boilers; valves, flanges, pumps, and compressors; storage and transfer of raw materials, products

and intermediates; waste water handling; flares; and emergency vents.

Although chemical manufacturing emissions vary depending on the specific process and related feedstok, the most common pollutants that may be emitted from point or fugitive sources during routine operations, include: carbon dioxide (CO_2), nitrogen oxides (NO_X), sulfur oxides (SO_X), ammonia (NH_3), acids and acid mists, chlorine gas, and dust Volatile organic compounds and tar fume are emitted from carbon black and coal tar distillation plants.

The gaseous emissions from the chemical manufacturing industry can be typically controlled by adsorption or absorption. Particulate emissions, usually less than 10 microns in aerodynamic diameter, are controlled by highly efficient systems such as bag filters, electrostatic precipitators, etc.

Chemical manufacturing facilities are large consumer of energy. Exhaust gas emissions produced by the combustion of gas or other fuels in turbines, boilers, compressors, pumps and other engines for power and heat generation, are a significant source of mainly CO_2 and NO_X.   Guidance for the management of small combustion source emissions with a capacity of up to 50 megawatt hours thermal (MWth), including air emission standards for exhaust emissions, is provided in the **General EHS Guidelines**. Guidance for the management of combustion source emissions from larger sources of power generation is provided in the EHS Guidelines for Thermal Power.

Greenhouse Gases (GHGs)

The LVIC manufacturing industry is a significant emitter of greenhouse gases, especially carbon dioxide (CO_2). GHGs are generated from the process as well as during the production of its highly demanding energy needs. Measures to increase

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energy efficiency and installation of Low NO$_X$ burners should be adopted since they will contribute to reduce CO_2 generation.

Attempts should be made to maximize energy efficiency and design facilities for lowest energy use. Recommendations on energy efficiency are addressed in the **General EHS Guidelines**.

Fugitive Emissions

Fugitive emissions are associated with leaks from pipes, valves, connections, flanges, packings, open-ended lines, floating roof storage tank and pump seals, gas conveyance systems, compressor seals, pressure relief valves, tanks or open pits / containments, and loading and unloading operations of products. Due to the presence of hazardous products in LVIC manufacturing facilities (i.e. NH$_3$ and chlorine), methods for controlling and preventing fugitive emissions should be considered and implemented in their design, operation, and maintenance. The selection of appropriate valves, flanges, fittings, seals, and packings should be based on their capacity to reduce gas leaks and fugitive emissions.

Use of open vents in tank roofs should be avoided by installing pressure relief valves. Storages and unloading stations should be provided with vapor recovery units. Vapor processing systems may consist of different methods, such as carbon adsorption, refrigeration, recycling collecting and burning.

Examples of measures for reducing the generation of fugitve emissions include:

- Rigorous maintenance programs, particularly in stuffing boxes on valve stems and seats on relief valves, to reduce or eliminate accidental releases;
- Selection of appropriate valves, flanges, fittings;
- Well designed, constructed, operated and maintained installations;

- Implementation of leak detection and repair programs;
- Installation of continuous monitoring in all sensitive areas.

Venting and Flaring

Venting and flaring are important safety measures used in chemical manufacturing facilities to ensure gas is safely disposed of during process start up and shut down or in the event of an emergency, power or equipment failure, or other plant upset conditions.

Recommended methods to prevent, minimize, and control air emissions from venting and flaring include:

- Use best practices and new technologies to minimize releases and potential impacts from venting and flaring (e.g., efficient flare tips, reliable pilot ignition system, minimization of liquid carry over, control of odor and visible smoke emissions, and locating flare at a safe distance from potential human and environmental receptors);
- Estimate flaring volumes and develop flaring targets for new facilities, and record volumes of gas flared for all flaring events;
- Divert gas emissions from emergency or upset conditions to an efficient flare gas system. Emergency venting may be acceptable under specific conditions where flaring of the gas stream is not possible, on the basis of a risk analysis. Justification for no gas flaring system should be fully documented before an emergency gas venting facility is considered.

Process Air Emissions – Ammonia Manufacturing

Process air emissions from ammonia plants consist mainly of hydrogen (H$_2$), carbon dioxide (CO_2), carbon monoxide (CO), and ammonia (NH$_3$). Concentrated carbon dioxide emissions are generated from CO_2 removal in these facilities. Fugitive emissions of NH$_3$ (e.g. from storage tanks, valves, flanges, and

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tubing) may also occur, especially during transport or transfer. Non-routine emissions associated with process upsets or accidents may contain natural gas, CO, H_2, CO_2, volatile organic compounds (VOCs), nitrogen oxides (NO_X) and NH_3.

Recommended emission prevention and control measures include the following:

- Use synthesis NH_3 purge gas treatment to recover NH_3 and H_2 before combustion of the remainder in the primary reformer;
- Increase the residence time for off-gas in the high-temperature zone;
- Connect ammonia emissions from relief valves or pressure control devices from vessels or tanks to a flare or to a water scrubber;
- Combine ammonia and urea facilities to reduce (through reuse in urea plant) ammonia process-generated CO_2 emissions[2]. Another industrial alternative is to combine with methanol production. It is noted that, in methanol production facilities, hydrogen is produced from natural gas, by means of a steam reforming unit followed by a methanol unit. This process, therefore, does not fully eliminate CO_2 emissions because of the energy used to run the hydrogen production and methanol synthesis units.

Process Air Emissions – Acid Manufacturing

Process emissions from acid plants include the following:

- Nitrous oxide (N_2O) and NO_X from nitric acid manufacturing plants, particularly from tail gas emissions[3];

- SO_2 resulting from incomplete oxidation and SO_3 resulting from incomplete absorption and droplets of sulfuric acid (H_2SO_4) from sulfuric acid manufacturing plants;
- Gaseous fluorides and dust from phosphoric / hydrofluoric acid plants;
- Hydrochloric acid (HCl) gas, chlorine, and chlorinated organic compounds resulting primarily from gases exiting the HCl purification system in HCl production;
- Fluorine, hydrofluoric acid (HF), and silicon tetrafluoride (SiF_4) from digestion of phosphate rock and dust from handling of phosphate rock in HF production. Particulate matter is emitted during handling and drying of the fluorspar. In hydrofluoric acid facilities fluorine emissions present in the final vents are typically very low following the required treatment

Recommended emission prevention and control measures include the following:

- The plant should be equipped with pre-condensers that remove water vapor and sulfuric acid mist, and with condensers, acid scrubbers, and water scrubbers that minimize the release of HF, SiF_4, SO_2, and CO_2 from the tail-gas;
- Use high-pressure adsorption process for nitric acid production to minimize the concentration of NO_X in the tail gas;
- Treat the off-gases from nitric acid plants using catalytic NO_X removal;
- Consider using double absorption process for H_2SO_4 plants. Plants operating on a single absorption process should consider implementation of the following:
  o Cesium catalyst in the last bed

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[2] Ammonia process-derived CO_2 can be almost totally consumed if the produced ammonia is transformed into urea (1t NH_3 - 1.5 t urea).

[3] The lowest NO_X emission levels currently achieved in a modern plant without added pollution abatement are between 1,000 to 2,000 ppmv for medium pressure absorption and 100 to 200 ppmv for high pressure absorption. For new plants in normal operating conditions the NO_X emission level (excluding N_2O)

can be at 100 ppmv, which is equivalent to 0.65kg NO_X (expressed as NO_2) per ton of 100% nitric acid produced.

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- o SO$_2$ abatement by scrubbing with a neutralizing compound
- o SO$_2$ abatement with hydrogen peroxide (H$_2$O$_2$)
- Control dust emissions from the flue-gases of directly heated dryers and/or from pneumatic conveying gases using cyclones and filters;
- Recover the fluorine as fluosilicic acid; a dilute solution of fluosilicic acid should be used as the scrubbing liquid. Fluorine, released during the digestion of phosphate rock and during the concentration of phosphoric acid, should be removed by scrubbing systems;
- Control emissions of HF by the condensing, scrubbing, and absorption equipment used in the recovery and purification of the hydrofluoric and hexafluorosilicic acid products;
- Minimize HF emissions, maintaining a slight negative pressure in the kiln during normal operations;
- Install caustic scrubbers to reduce the levels of pollutants in the HF tail-gas, as needed;
- Control dust emissions by bag filters at the fluorspar silos and drying kilns. Collect dust from the gas streams exiting the kiln in HF production and return the dust to the kiln for further processing;
- Control dust emissions from fluorspar handling and storage with flexible coverings and chemical additives, and
- Control dust emissions from phosphate rock during transport, handling and storage, using enclosed systems and bag filters.

Process Air Emissions – Chlor-Alkali Plants

The principal chlor-alkali processes are mercury, diaphragm, and membrane cell electrolysis. The most significant emissions from all three processes are both fugitive and point source chlorine gas emissions. Sources of potential significant chlorine emissions are normally associated with the chlorine destruction unit where emissions from non-condensable gases remaining

from liquefaction (H$_2$, O$_2$, N$_2$, CO$_2$) having a chlorine content from 1-8% of the raw chlorine gas produced are treated. Other emissions from chlor-alkali plants are linked to the brine purification. Air emissions from mercury cell technology include mercury vapors, emitted as fugitive emissions from the cells (e.g. cell room ventilation gas).

Principal air emissions from soda ash manufacturing are process carbon dioxide and particulate emissions from ore calciners, soda ash coolers and dryers, ore crushing, screening, and transportation operations, product handling and shipping operations. Emissions of products of combustion, such as carbon monoxide, nitrogen oxides, and sulfur dioxide, occur from direct-fired process heating units such as ore calcining kilns and soda ash dryers. Ammonia may also be emitted. Nitrogen oxides are produced in small quantities inside the kiln by the oxidation of nitrogen contained in the air used in the combustion process, and sulfur oxides by the oxidation of compounds containing sulfur in the limestone.

Recommended emission prevention and control measures include the following:

- Discontinue use of mercury and diaphragm cell processes, where possible, and adopt new membrane cell process. Alternatively, install improved cell part materials (e.g. dimensionally stable anodes (DSA®), modified diaphragm), as needed;
- Prepare mercury mass balances to account for all mercury use;
- Optimize process to keep the cells as close as possible;
- Install mercury distillation units to recover mercury;
- Ensure that that the mercury cell end boxes and caustic boxes are properly sealed, thus eliminating fugitive releases;

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- Design the chlorine absorption unit with a treatment capacity sufficient to absorb the full cell-room production and prevent emissions of chlorine gas in the event of a process upset until the plant can be shut down. The absorption unit should be designed to lower the chlorine content in the emitted gas to less than 5 mg/m³ in the worst case scenario;

- Direct all chlorine-containing waste gas streams to the chlorine absorption unit and ensure that the system is gas tight;

- Install chlorine gas detectors in areas with a potential risk of chlorine leaks to allow for immediate leakage detection;

- Use carbon tetrachloride-free chlorine liquefaction and purification processes. The use of carbon tetrachloride (CCl_4), for removal of nitrogen trichloride (NCl_3) and for absorption of tail gas, should be avoided and discontinued;

- In soda ash facilities, control particulate emissions from ore and product handling operations by either venturi scrubbers, or baghouse filters, electrostatic precipitators, and/or cyclones and recycle the collected particulates.

Process Air Emissions – Carbon Black Manufacturing

An important potential source of emission to air is the tail gas coming from the reactor after carbon black separation, which is a low calorific gas with a high moisture content due to the quench water vapor. The tail-gas composition may vary considerably according to the grade of carbon black being produced and the feedstock used. It may contain H_2, CO, CO_2, reduced sulfur compounds (H_2S, CS_2 and COS), SO_2, nitrogen compounds (N_2, NO_X, HCN and NH_3), VOCs such as ethane and acetylene, and carbon black particles that are not captured by product separation bag filters.

Recommended emission prevention and control measures include the following:

- Use primary feedstock with a sulfur content in the range of 0.5 - 1.5 percent[4];

- Preheat process air in heat exchangers using the hot gases (containing carbon black) leaving the furnace black reactor;

- Install and maintain high-performance bag filters to ensure high carbon black collection efficiency and minimum product losses of the residual carbon black in the filtered tail gas;

- Utilize the energy content of the tail gas (by burning the gas and using the energy produced);

- Primary NO_X reduction techniques should be applied to reduce the NO_X content in flue-gas originating from tail-gas combustion in energy producing systems [5];

- Install fabric filters for the air conveying system, vent collection system, and dryer purge gas[6];

- Vent un-combusted tail-gas only during emergencies, start-up and shut-down periods, and during periods of grade change.

Process Air Emissions – Coal Tar Distillation

Although coal tar distillation emissions occur in normal operating conditions, the key emissions from these processes that warrant control are those consisting of tar fume, odor, polycyclic aromatic hydrocarbons (PAH), and particulate matter, which may originate from facility processes including delivering, storing, heating, mixing, and cooling tar.

Recommended emission prevention and control measures include the following:

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[4] Specific emission levels of 10 – 50 kg SO_X (as SO_2) per tonne of rubber grade carbon black produced are possible, as a yearly average.

[5] Plants emission levels associated with use of BAT are less than 0.6 g NO_X/Nm³ as an hourly average at 3 % O_2 during normal production.

[6] For the low temperature air conveying and vent collector systems, associated emission levels are 10 to 30 mg/Nm³ as a half-hour average. For the dryer purge filter, associated emission levels are from less than 20 to 30 mg/Nm³ as a half-hour average

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- Use ground-based pumps and other methods to optimize tar deliveries to reduce emissions of tar fume and odor;

- Site storage tanks downwind of potential nearby receptors, control temperature of stored materials[7], and implement careful handling procedures to prevent odor nuisance;

- Implement overfill prevention methods for bulk storage tanks, such as high-level alarms or volume indicators;

- Used local exhaust ventilation adequate to collect and treat VOC emissions from mixing tanks and other processing equipment.

Liquid Effluents

Liquid effluents include process and cooling water, storm water, and other specific discharges (e.g. hydrotesting and cleaning, mainly during facility start up and turnaround).[8] Process water discharges from LVIC manufacturing plants may include the acid wash from scheduled cleaning activities and purges, which are part of daily operation. Additional potential sources of effluents may include scrubbers, if used as air emission control systems. Accidental releases or leaks from product storage tanks such as refrigerated ammonia and acid storage may also produce effluents. Other sources include acidic and caustic effluents from the boiler feed water preparation for the different steam systems. Cooling water and storm water management are addressed in the **General EHS Guidelines**.

Effluents and control specific to different types of chemicals manufacturing plants are described below.

Effluents – Ammonia Manufacturing

Plant discharges, during normal operation, may occur due to process condensates or due to the scrubbing of waste gases containing ammonia and other products. In partial oxidation,

soot and ash removal may impact water discharged, if not properly handled.

Recommended measures to prevent, minimize, and control effluents from ammonia plants include:

- Recover ammonia absorbed from purge and flash gases in a closed loop system so that no aqueous ammonia emissions occur;

- Recover soot from gasification in partial oxidation processes and recycle the recovered material to the process.

Effluents – Acids Manufacturing

Effluents from nitric acid plants may be contaminated with nitrogen compounds. Effluents from hydrochloric acid plants can vary depending on manufacturing processes from traces of HCl when reacting H_2 with Cl, to mineral salt (Na_2SO_4) when the acid is produced by reacting sodium chloride with sulfuric acid.

Liquid releases from phosphoric acid plants mainly consist of the liquid effluents originating from vacuum cooler condensers and gas scrubbing systems used for condensation and cleaning of the vapors that evolve in the various process stages. These condensed acidic vapors contain mainly fluorine and small amounts of phosphoric acid. The fluorine released from the reactor and evaporators can be recovered as a commercial by-product (fluorosilicic acid 20-25 percent).

Recommended measures to prevent, minimize, and control effluents from acid plants include:

- Use closed-loop reactors and evaporators to eliminate process wastewater;

- Recirculate the water used for the transport of phosphogypsum into the process after settling;

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[7] The rate of fume emission doubles for approximately every 11ºC rise in temperature.

[8] Facility turnarounds are usually limited to once every three to four years and last a few weeks.

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- Treat scrubber effluent with lime or limestone or use seawater as a scrubbing liquid to precipitate fluorine as calcium fluoride;

- Install a separator to remove phosphoric acid droplets from vacuum flash coolers and vacuum evaporators emissions before scrubbing to minimize contamination of the scrubber effluent with phosphorous pentoxide (P_2O_5);

- Recover fluorosilicic acid (H_2SiF_6) from treatment of tail gases from hydrofluoric units for use as a feed material or for the manufacture of fluorides or silicofluorides. H_2SiF_6 can also be chemically combined to produce CaF_2 and silica.

Effluents – Chlor-Alkali Plants

Brine is one of key waste streams of the chlor-alkali industry. Membrane cells may use recycled brine requiring dechlorination. Specifically for membrane technology, brine purification is of critical importance to long membrane life and high efficiency. The main components in brine purification wastes are sulfate, chloride, free oxidants, chlorate, bromate, and carbon tetrachloride.

The main sources of liquid effluent from the soda ash process are typically waste water from the distillation and brine purification and cooling waters. The effluents are characterized by high levels of suspended solids[9]. Another significant issue is the potential discharge of heavy metals present in the main raw materials[10].

Recommended measures to prevent, minimize, and control effluents from chlor-alkali plants include:

- Purify brine by pH adjustment, precipitation, flocculation and filtration to keep impurities at acceptable levels. The consumption of chemicals which are employed to purify the brine varies from plant to plant depending on the impurities of the brine;

- Recycle brine in membrane technology, removing impurities by ion exchange resin units. Regeneration of resins requires caustic soda and acid washing;

- Minimize consumption and discharge of sulfuric acid by means of on-site re-concentration in closed loop evaporators. The spent acid should be used to control pH in process and waste water streams; resold to a user that accepts this quality of acid; or returned to a sulfuric acid manufacturer for re-concentration;

- Use fixed bed catalytic reduction, chemical reduction, or other equally effective method to minimize discharge of free oxidants[11];

- Adopt carbon tetrachloride-free chlorine liquefaction and purification processes;

- Use acid conditions in the anolyte (pH 1-2) to minimize the formation of chlorate (ClO_3) and bromate (BrO_3), and chlorate destruction in the brine circuit to remove chlorate before purging in membrane plants[12].

Effluents – Carbon Black / Coal Tar Distillation

Wastewater effluents are of relatively limited significance for the carbon black industry and in coal tar distillation units.

A zero discharge to water is possible for some types of carbon black plants. However, the production of some rubber black and nearly all specialty black grades require clean quench water. Suspended solids (mainly carbon black) should be filtered

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[9] Loads of suspended solids discharged with waste waters are generally significant and range from 90 to 700 kg/t soda ash, with an average value estimated at 240 kg/t soda ash.

[10] For a soda ash plant with a capacity of around 600 kt/year, 10 tonnes per year can be reached.

[11] The emission level of free oxidants to water associated with implementation of best available technuiques is less than 10 mg/l.

[12] The chlorate level associated with best available techniques in the brine circuit is 1-5 g/l and the associated bromate level is 2-10 mg/l, and depends on the bromide level in the salt.

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before discharge (or re-use) to levels less than 20 mg/l. After filtration, process streams can be reused.

Suspended solids, BOD and PAH concentrations should be monitored in effluents from coal tar distillation units.

Hydrostatic Testing Water

Hydrostatic testing of equipment and pipelines usually needs significant amount of water (e.g., NH$_3$ tanks may have capacities of more than 20-30,000 m^3). Chemical additives (typically a corrosion inhibitor, an oxygen scavenger, and a dye) are often added to the water to prevent internal corrosion.

In managing hydrotest waters, pollution prevention and control measures should be considered including: optimizing water consumption and optimum dosage and careful selection of needed chemicals.

If discharge of hydrotest waters to the sea or to surface water is the only feasible alternative, a hydrotest water disposal plan should be prepared. The plan should include, at a minimum, characteristics of the discharge point(s) rate of discharge, chemical use and dispersion, environmental risk, and required monitoring.

Hydrotest water disposal into shallow coastal waters should be avoided.

Wastes

Well-managed chemicals manufacturing plants should not generate significant quantities of solid wastes during normal operation. Typical wastes generated include waste oils, spent catalysts, sludge from wastewater treatment units, collected dust from bag houses, bottom ashes from boilers, muds and cakes from filtration units, etc.

Recommended management strategies for spent catalysts include the following:

- Proper on-site management, including submerging pyrophoric spent catalysts in water during temporary storage and transport until they reach the final point of treatment to avoid uncontrolled exothermic reactions;
- Off-site management by specialized companies that can recover and recycle heavy metals (or precious metals from nitric acid plant catalysts) whenever possible.

Storage and handling of hazardous and non-hazardous wastes should be conducted in a way consistent with good EHS practice for waste management, as described in the **EHS General Guidelines**.

Waste – Ammonia Manufacturing

Ammonia manufacturing processes should not produce significant solid wastes[13]. Spent catalysts and molecular sieves management should be conducted as specified above.

Waste – Acids Manufacturing

Phosphogypsum is the most significant by-product in wet phosphoric acid production[14]. Phosphogypsum contains a wide range of impurities, some of which are considered a potential hazard to the environment and public health.[15,16]

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[13] Spent catalysts and other solid waste should be less than 0.2kg per ton of product.

[14] Around 4 - 5 tons of phosphogypsum (principally calcium sulfate, CaSO4) are produced for every ton of phosphoric acid produced

[15] The impurities contained in the phosphate rock are distributed between the phosphoric acid produced and the calcium sulfate (gypsum); mercury, lead and radioactive components, where present, end up mainly in the gypsum, while arsenic and the other heavy metals such as cadmium end up mainly in the acid. The radioactivity of phosphate rock is mainly from radionuclides from the radioactive decay series of uranium-238.

[16] Phosphate rock, phosphogypsum, and the effluents produced from a phosphoric acid plant have generally a lower radioactivity than the exemption values given in the relevant international regulations and guidelines (for example, EU Directive 96/26/EURATOM)

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Calcium sulfate (anhydrite) is produced as a by-product of hydrofluoric acid (HF) manufacturing, containing between 0.2 to 2.0 % of unreacted CaF_2 and less than 1.0 % H_2SO_4. It also contains the majority of the trace impurities contained in the fluorspar[17].

Recommended measures to prevent or minimize solid waste generation and to manage solid waste from acid plants include:

- Disposal of phosphogypsum in land facilities designed to prevent leaching to groundwater or surface water. Any effort should be made in order to reduce the impact of phosphogypsum disposal and possibly improve the quality of the gypsum, for its reuse. Disposal to sea is considered non acceptable;
- Refinement and sale of calcium sulfate anhydrite from HF production for use in other products (e.g. cement), if possible.

Waste – Chlor-Alkali Plants

Brine sludges are one of the largest waste streams of the chlor-alkali industry. The quantity of brine filtration sludges mainly depends on the incoming salt characteristics, used for the purification of the brine. The precipitated salts are removed from the brine through decantation/clarification and filtration. The sludge may be removed discontinuously by flushing with a weak hydrochloric acid solution. The acid causes the precipitate to dissolve and the relatively harmless solution can be discharged with liquid effluent. Wastes are generated during the secondary brine purification and consist of used materials such as precoat and body feed material made of cellulose. The precoat filter sludge from the brine softener consists mainly of alpha-cellulose, contaminated with iron hydroxide and silica[18]. Ion

exchange resins for secondary brine purification are rarely changed[19]. Spent membranes[20] and gaskets from membrane cells are other waste streams.

The main solid wastes from soda ash unit are fines of limestone (30 – 300 kg/t soda ash) and non recycled grits at slaker (10 – 120 kg/t soda ash).

Recommended measures to prevent, minimize solid waste generation and to manage solid waste from chlor-alkali plants include:

- Attempt to find reuse options for waste solids from the purification of salt brine; if the waste must be disposed of, consider the use of natural repositories, such brine cavities;
- Select limestone with high $CaCO_3$ content, appropriate physical characteristics, and limited content of heavy metals and other impurities.

Waste – Carbon Black / Coal Tar Distillation

Carbon black processes generate very limited amount of hazardous waste (oil residues). Coal-tar pitch is a black solid residue from the distillation of coal tar. The recovery of tar chemicals leaves residual oils, including heavy naphtha, dephenolated carbolic oil, naphthalene drained oil, wash oil, strained anthracene oil, and heavy oil.

Recommended measures to prevent, minimize solid waste generation and to manage solid waste include:

- Reuse spent oil, oil sludge, and coal tar distillation residues as feedstock or fuel, if possible;
- Recycle off-specification carbon black back into the process.

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[17] About 3.7 tonnes of anhydrite per tonne of HF are produced as by-product.
[18] Membrane cell plants report a figure of 600 g/t for sludge from brine softening.

[19] Resins are regenerated about 30 times per year.
[20] The membranes have a lifetime of between 2 and 4 years.

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Hazardous Materials Management

Chemical manufacturing plants are required to assess the risks associated with the use and handling of hazardous materials and implement practices to prevent and minimized such risks. As indicated in the **General EHS Guidelines**, the application of these management practices should be documented in a written Hazardous Materials Management Plan[21]. The purpose of this plan is to establish and implement a systematic set of preventive actions against accidental releases of substances that can cause serious harm to the public and the environment from short-term exposures and to mitigate the severity of releases that do occur.

Industry-specific pollution prevention and control practices include the following:

- Accidental releases of fluids through should be prevented trough inspections and maintenance of storage and conveyance systems, including stuffing boxes on pumps and valves and other potential leakage points. Spillages of dangerous intermediates and product should be contained and recovered or neutralized as quick as possible;
- Secondary containment for the storage tanks storing liquids (i.e, ammonia, acids, etc.) and spare capacity for dangerous products like chlorine should be installed as discussed in the **General EHS Guidelines**;
- Maintain good housekeeping practices, including conducting product transfer activities over paved areas and prompt collection of small spills.

Noise

In chemical manufacturing facilities, significant noise sources include large size rotating machines, such as compressors and turbines, pumps, electric motors, air coolers, and fired heaters.

During emergency depressurization, high noise levels can be generated due to high pressure gases to flare and/or steam release into the atmosphere.

Noise prevention and abatement strategies include:

- Optimization of plant layouts in order to use the larger buildings as noise barriers and locating noise sources as far as possible from existing receptors;
- Use of low noise generation equipment;
- Installation of acoustic insulating barriers and silencers.

Noise abatement and control measures are similar to other large industries and are addressed in the **General EHS Guidelines.**

Odors

Odors from fugitive vapor releases or from wastewater treatment plants may be generated in the LVIC manufacturing processes. Adequate controls to eliminate leaks should be implemented to minimize fugitive releases and prevent odor nuisances.

Decommissioning

Chemical manufacturing facilities may have important quantities of solid and liquid hazardous materials such as CO_2 removal solutions, liquid ammonia, chlorine, soda, acids and products in process and storage systems, off spec products, spent catalysts, and mercury from mercury cell chlor-alkali plants.

Recommended management practices of decommissioning activities include the following:

- In the case of mercury cell chlor-alkali plants, carefully plan all decommissioning steps to minimize releases of mercury and other hazardous substances (including dioxins and furans if graphite anodes were used) and to protect worker

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[21] See IFC Hazardous Waste Management Manual.

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health and safety, and plan for disposition of the remaining mercury;

- Collect CO_2 removal solutions in the ammonia plants and all dangerous products for further handling and disposal as a hazardous waste material;

- Remove spent catalysts from NH_3 and HNO_3 plants for further management as described in the solid waste section above;

- Recover and further manage NH_3, Cl_2, acids, and all other products from the synthesis section and storage tanks as well as all products and intermediates from the storage tanks according to hazardous materials management guidance from the **General EHS Guidelines.**

General guidance on decommissioning and contaminated land remediation is provided in the **General EHS Guidelines**.

1.2   Occupational Health and Safety

The occupational health and safety issues that may occur during the construction and decommissioning of LVIC facilities are similar to those of other industrial facilities, and their management is discussed in the **General EHS Guidelines**. Facility-specific occupational health and safety issues should be identified based on job safety analysis or comprehensive hazard or risk assessment, using established methodologies such as a hazard identification study [HAZID], hazard and operability study [HAZOP], or a quantitative risk assessment [QRA]. As a general approach, health and safety management planning should include the adoption of a systematic and structured approach for prevention and control of physical, chemical, biological, and radiological health and safety hazards described in the **General EHS Guidelines**.

In addition, occupational health and safety issues for specific consideration in chemical operations include:

- Chemical hazards due to acute and chronic exposure to toxic gases and other hazardous compounds;

- Major hazards, including fires and explosions.

Major hazards should be managed according to international regulations and best practices (e.g., OECD Recommendations[22], EU Seveso II Directive[23] and USA EPA Risk Management Program Rule[24]).

Chemical Hazards

The industry is characterized by the presence of toxic compounds, including chlorine gas, ammonia, acids, caustic soda, amines, components of coal tar (e.g. mononuclear and polycyclic aromatic hydrocarbons, phenols, and pyridine bases), which can be toxic when ingested, inhaled, or absorbed through the skin. The main health hazard usually associated with coal tar and its products is carcinogenicity due to long-term, continued exposure of the skin to finely divided solid pitch (dust).

Recommendations to prevent, minimize, or control occupational health impacts from exposure to toxic substances at these facilities include:

- Assess and minimize the concentrations of toxic substances in working areas in both normal and emergency conditions. Rigorous workplace monitoring protocols ought to be in place as part of the overall occupational and health and safety management system. Protective clothing, including eye protection and PVC gloves, should be worn, suitable respirators be available, and regular medical checkups be carried out on all personnel, as needed;

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[22] OECD, Guiding Principles for Chemical Accident Prevention, Preparedness and Response, Second Edition (2003).
[23] EU Council Directive 96/82/EC, so-called Seveso II Directive, extended by the Directive 2003/105/EC.
[24] EPA, 40 CFR Part 68, 1996 - Chemical accident prevention provisions.

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- Install gas detectors in hazard areas, wherever possible. For example, chlorine detectors should be placed in areas of potential risk of chlorine leaks, giving immediate indication of the presence and location of any leakage;

- Ensure effective ventilation, where the lower boiling products are handled;

- Provide and use barrier creams formulated against aromatic hydrocarbons.

Major Hazards

The most significant safety impacts are related to the handling and storage of NH$_3$ (volatile and poisonous in high concentrations), chlorine (highly poisonous), caustic soda, nitric, hydrochloric, sulfuric, hydrofluoric, phosphoric acids and organic compounds and combustible gases such as natural gas, CO, and H$_2$ and other process chemicals. These impacts may include significant acute exposures to workers and, potentially, to surrounding communities, depending on the quantities and types of accidentally released chemicals and the conditions for reactive or catastrophic events, such as fire and explosion.

LVIC manufacturing facilities may generate or process large quantities of combustible gases, such as natural gas, H$_2$, CO, and other process chemicals. Synthetic Gas (SynGas; containing H$_2$ and CO[25]) generated at ammonia plants may cause "Jet Fires" if ignited in the release section, or give rise to Vapor Cloud Explosion, "Fireballs," or "Flash Fires," depending on the quantity of flammable material involved, the degree of confinement of the cloud, and the congestion of the area interested by the flammable cloud.

The risk of fire, explosion and other major hazards should be minimized through the following measures:

- Establishing a plant layout to reduce the frequency of product transfers and the likelihood of accidental releases, as well as to facilitate the collection of accidental releases;

- Early detection of the release;

- Limiting the inventory which may be released by isolation of the installation from large inventories and isolation and blow-down of pressurized flammable gases inventories. Process areas, storage areas, utility areas, and safe areas should be segregated, preferably by adoption of safety distances. These distances can be derived from safety analyses specific for the facility, considering the occurrence of the hazards or from applicable standards or guidelines (e.g., API, NFPA);

- Removing potential ignition sources;

- Removing or diluting the release and limiting the area affected by the loss of containment.

Recommended industry specific measures to minimize the above mentioned risks include:

- Minimize the liquid chlorine inventory and the length of pipeline containing liquid chlorine;

- Design atmospheric ammonia storage tanks (- 33°C) with dual walls and an external concrete wall with the roof resting on the outer wall, and using an adequate margin between operating and relief pressure. Refrigerated storage should be preferred for storage of large quantities of liquid ammonia, since the initial release of ammonia in the case of a line or tank failure is slower than with pressurized ammonia storage systems;

- Design chlorine storage tanks based on a specific analysis of major failure or accident risks and consequences, and accounting on the possibility to safely recover and handle any product spills—consider low-temperature storage (-34°C) for large storage capacities, and provision of at least

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[25] Hydrogen and carbon monoxide have autoignition temperatures of 500°C and 609°C, respectively; therefore in some points of the SynGas generation unit, where gas temperature is higher, potential gas releases may self ignite without the need of ignition sources.

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one empty tank equal in capacity to the largest chlorine
storage tank as an emergency spare;

- Given their highly corrosive and toxic nature, special
  attention should be given to the handling and storage of
  acids including prevention of leaks or spills to effluent
  waters by provision of secondary containment; separation
  from critical drainage channels; and continuous monitoring
  and alarm detection systems (such as automatic pH
  monitoring) of at-risk containment and drainage networks;

- Avoid pressurizing for unloading large quantities of nitric
  acid. The recommended material for tanks, vessels and
  accessories is low carbon austenitic stainless steel;

- Only use specially trained and certified staff or contractors
  for deliveries and transfer of all process chemicals,
  including chemicals used in the CO_2 removal unit of the
  ammonia plant.

1.3   Community Health and Safety

Community health and safety impacts during the construction
are common to those of most industrial facilities, and are
discussed in the **General EHS Guideline**. These impacts
include, among other things, dust, noise, and vibration from
construction vehicle transit, and communicable disease
associated with the influx of temporary construction labor.

The most significant community health and safety hazards
during the operation of chemical facilities are related to:

- Handling and storage of hazardous materials including raw
  materials, intermediaries, products and wastes near
  populated areas;

- Shipping of hazardous products (ammonia, chlorine, acids,
  carbon black), with possibility of accidental leak of toxic
  and flammable gases;

- Disposal of solid waste (phosphogypsum, sludge).

The design should include safeguards to minimize and control
hazards to the community, through the following:

- Identifying reasonable design leak cases;

- Assessing the effects of the potential leaks on the
  surrounding areas, including groundwater and soil
  pollution;

- Properly selecting the plant location in respect to the
  inhabited areas, meteorological conditions (e.g. prevailing
  wind directions), and water resources (e.g., groundwater
  vulnerability) and identifying safe distances between the
  plant area and the community areas; and

- Identifying the prevention and mitigation measures required
  to avoid or minimize the hazards.

If the facilities are located on the shore, the ship traffic
associated with the facilities should be considered in the
assessment, analyzing the potential impact of the traffic on the
local marine traffic and activities and the potential impacts of
liquids leaks from the unloading or offloading operations.
Measures to avoid accidental impacts and minimize disturbance
to other marine activities in the area should be assessed. Risk
analysis and emergency planning should include, at a minimum,
the preparation of an Emergency Management Plan, prepared
with the participation of local authorities and potentially affected
communities. Other community health and safety hazards are
common to those of most large industrial facilities, and are
discussed in the **General EHS Guideline**.

Community health and safety impacts during the
decommissioning are common to those of most large industrial
facilities, and are discussed in the **General EHS Guideline**.
These impacts include, among other things, transport safety,
disposal of demolition waste that may include hazardous
materials, and other impacts related to physical conditions and
the presence of hazardous materials after site abandonment.

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Guidance for the management of these issues at chemical plants is presented under Section 1.2 and in relevant sections of the **General EHS Guidelines** including "Planning, Siting, and Design", and "Emergency Preparedness and Response".

2.0 Performance Indicators and Monitoring

2.1 Environment

Emissions and Effluent Guidelines

Tables 1 and 2 present emission and effluent guidelines for this sector. Guideline values for process emissions and effluents in this sector are indicative of good international industry practice as reflected in relevant standards of countries with recognized regulatory frameworks. These levels should be achieved, without dilution, at least 95 percent of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours. Deviation from these levels in consideration of specific, local project conditions should be justified in the environmental assessment.

Effluent guidelines are applicable for direct discharges of treated effluents to surface waters for general use. Site-specific discharge levels may be established based on the availability and conditions in the use of publicly operated sewage collection and treatment systems or, if discharged directly to surface waters, on the receiving water use classification as described in the **General EHS Guideline**.

Emissions guidelines are applicable to process emissions. Combustion source emissions guidelines associated with steam and power generation activities from sources with a capacity equal to or lower than 50 thermal megawatts are addressed in the **General EHS Guideline** with larger power source emissions addressed in the **EHS Guidelines for Thermal Power**.

Guidance on ambient considerations based on the total load of emissions is provided in the **General EHS Guideline**.

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Table 1. Air Emissions Levels		
Pollutant	**Units**	**Guideline Value**
Ammonia Plants		
NH_3	mg/Nm^3	50
NO_x	mg/Nm^3	300
Particulate Matter	mg/Nm^3	50
Nitric Acid Plants		
NO_x	mg/Nm^3	300
N_2O	mg/Nm^3	800
NH_3	mg/Nm^3	10
Sulfuric Acid Plants		
SO_2	mg/Nm^3	450 (2 kg/t acid)
SO_3	mg/Nm^3	60 (0.075 kg/t acid)
H_2S	mg/Nm^3	5
NO_x	mg/Nm^3	200
Phosphoric / Hydrofluoric Acids Plants		
Fluorides (gaseous) as HF	mg/Nm^3	5
Particulate Matter/CaF_2	mg/Nm^3	50 (0.10 kg/t phosphate rock)
Chlor-alkali / Hydrochloric Acid Plants		
Cl_2	mg/Nm^3	1 (partial liquefaction) 3 (complete liquefaction
HCl	ppmv	20
Hg	mg/Nm^3	0.2 (annual average emission of 1 g/t chlorine)
Soda Ash Plants		
NH_3	mg/Nm^3	50
H_2S	mg/Nm^3	5
NO_x	mg/Nm^3	200
Particulate Matter	mg/Nm^3	50
Carbon Black		
SO_2	mg/Nm^3	850
NO_x	mg/Nm^3	600
CO	mg/Nm^3	500
Particulate Matter	mg/Nm^3	30
VOC	mg/Nm^3	50
Coal Tar Distillation		
Tar fume	mg/Nm^3	10
VOC	mg/Nm^3	50
Particulate Matter	mg/Nm^3	50

Table 2. Effluent Levels		
Pollutant	**Units**	**Guideline Value**
pH	S.U.	6-9
Temperature Increase	°C	<3
Ammonia Plants		
NH_3	mg/l	10 (0.1 kg/t) [1]
TSS	mg/l	30
Nitric Acid Plants		
NH_3	mg/l	10
Nitrates	g/t	25
TSS	mg/l	30
Sulfuric Acid Plants		
Phosphorus	mg/l	5
Fluoride	mg/l	20
TSS	mg/l	30
Phosphoric Acid Plants		
Phosphorus	mg/l	5
Fluoride	mg/l	20
TSS	mg/l	30
Hydrofluoric Acid Plants		
Fluorides	kg/tonne HF	1
Suspended Solids	kg/tonne HF	1
	mg/l	30
Chlor-alkali /Hydrochloric Acid Plant		
TSS	mg/l	20 [2]
COD	mg/l	150 [2]
AOX	mg/l	0.5 [2]
Sulfides	mg/l	1
Chlorine	mg/l	0.2 [2]
Mercury	--	0.05 mg/l 0.1 g/t chlorine
Toxicity to Fish Eggs	T_F	2
Soda Ash Plants		
Suspended solids	kg/t	270
Phosphorus	kg/t	0.2
TSS	mg/l	30
Ammonia (as N)	mg/l	10
Carbon Black Plants		
COD	mg/l	100
Suspended Solids	mg/l	20
Coal Tar Distillation Plants		
BOD_5	mg/l	35 (monthly average) 90 (daily maximum)
TSS	mg/l	50 (monthly average) 160 (daily maximum)
Anthracene, Naphthalene and Phenanthrene (each)	µg/l	20 (monthly average) 60 (daily maximum)

Notes:
1. Load based guideline: 0.1 kg/t of product
2. Non-asbestos diaphragm plants

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Resource Use, Energy Consumption, Emission and Waste Generation

Tables 3 and 4 provide examples of resource consumption and waste generation benchmarks in this sector. Industry benchmark values are provided for comparative purposes only and individual projects should target continual improvement in these areas.

Notes:
1. European Fertilizer Manufacturers Association (EFMA). 2000.
2. EU IPPC - Reference Document on Best Available Techniques in Large Volume Inorganic Chemicals - Solid and Others industry. December 2006.
3. EU IPPC - Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing industry December 2001.
4. EU IPPC - Reference Document on Best Available Techniques in Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilizers Industries. October 2006.

Table 3. Resource and Energy Consumption		
Product	**Unit**	**Industry Benchmark**
Ammonia	GJ lower heating value (LHV)/tonne NH_3	28.8 to 31.5[1]
Phosphoric Acid	Tonne phosphate rock/tonne P_2O_5	2.6-3.5 [1]
	KWh/tonne P_2O_5	120-180 [1]
	m^3 cooling water/tonne P_2O_5	100-150 [1]
Hydrofluoric Acid	Tonne CaF_2/tonne HF	2.1-2.2 [4]
	Tonne H_2SO_4/tonne HF	2.6-2.7 [4]
	KWh/tonne HF	150-300 [4]
Chlor-Alkali	KWh/tonne Cl_2	3000 without Cl liquefaction 3200 with Cl liquefaction / evaporation[3]
	Tonne NaCl/tonne Cl_2	1.750 [3]
	g Hg/tonne of chlorine capacity (mercury cell plants)	0.2-0.5 [3]
Soda Ash	GJ/tonne soda ash	9.7-13.6[2]
	Tonne limestone/tonne soda ash	1.09-1.82 [2]
	Tonne NaCl/tonne soda ash	1.53-1.80[2]
	m^3 cooling water/tonne soda ash	50-100 [2]
Carbon Black	KWh/tonne carbon black	430-550[2]
	GJ/tonne carbon black	1.55-2 [2]

Table 4. Emissions, Effluents and Waste Generation		
Parameter	**Unit**	**Industry Benchmark**
Ammonia Plants		
CO_2 from process	tonne/tonne NH_3	1.15-1.3 [1]
NO_X (advanced conventional reforming processes and processes with reduced primary reforming)	kg/tonne NH_3	0.29 – 0.32
NO_X (heat exchange autothermal reforming)	kg/tonne NH_3	0.175
Nitric Acid Plants		
N_2O	kg/tonne 100% HNO_3	0.15-0.6 [4]
NO_X	ppmv	5-75 [4]
Sulfuric Acid Plants		
SO_2 (Sulfur burning, double contact/double absorption)	mg/Nm^3	30-350 [1][4]
SO_2 (Single contact/single absorption)	mg/Nm^3	100-450[4]
Phosphoric / Hydrofluoric Acid Plants		
Fluorides	mg/Nm^3	0.6-5[4]
SO_2	kg/tonne HF	0.001 – 0.01[4]
Solid Waste (phosphogypsum)	tonne/tonne P_2O_5	4-5 [1]
Anhydrite ($CaSO_4$)	tonne/tonne HF	3.7 [4]
Chlor Alkali Plants		
Cl_2 (partial liquefaction)	mg/Nm^3	<1 [3]
Cl_2 (total liquefaction)	mg/Nm^3	<3 [3]
Chlorates (brine circuit)	g/l	1-5 [3]
Bromates (brine circuit)	mg/l	2-10 [3]
Soda Ash Plants		
CO_2	Kg/tonne soda ash	200-400 [2]
Cl	Kg/tonne soda ash	850-1100 [2]

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Ca	Kg/tonne soda ash	340-400 [2]
Na	Kg/tonne soda ash	160-220 [2]
Waste water/suspended solids	m^3/tonne/ tonne soda ash	8.5-10.7/ 0.09-024 [2]
Carbon Black Plants		
SO$_2$	kg/tonne of rubber grade carbon black	10-50 [2]
NO$_X$	mg/Nm^3	<600 [2]
VOC	mg/Nm^3	<50 [2]

Table 4 Notes:
1. European Fertilizer Manufacturers Association (EFMA). 2000;
2. EU IPPC - Reference Document on Best Available Techniques in Large Volume Inorganic Chemicals - Solid and Other Industries. Dec, 2006.;
3. EC IPPC - Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing industry December 2001;
4. EC IPPC - Referenc e Document on Best Available Techniques in Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilizers Industries. Oct, 2006.

Environmental Monitoring

Environmental monitoring programs for this sector should be implemented to address all activities that have been identified to have potentially significant impacts on the environment, during normal operations and upset conditions.   Environmental monitoring activities should be based on direct or indirect indicators of emissions, effluents, and resource use applicable to the particular project.

Monitoring frequency should be sufficient to provide representative data for the parameter being monitored. Monitoring should be conducted by trained individuals following monitoring and record-keeping procedures and using properly calibrated and maintained equipment. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Additional guidance on applicable sampling and analytical methods for emi ssions and effluents is provided in the **General EHS Guidelines**.

2.2   Occupational Health and Safety Performance

Occupational Health and Safety Guidelines

Occupational health and safety performance should be evaluated against internationally published exposure guidelines, of which examples include the Threshold Limit Value (TLV®) occupational exposure guidelines and Biological Exposure Indices (BEIs®) published by American Conference of Governmental Industrial Hygienists (ACGIH),[26] the United States National Institute for Occupational Health and Safety (NIOSH),[27] Permissible Exposure Limits (PELs) published by the Occupational Safety and Health Administration of the United States (OSHA),[28] Indicative Occupational Exposure Limit Values published by European Union me mber states,[29] or other similar sources.

Accident and Fatality Rates

Projects should try to reduce the number of accidents among project workers (whether directly employed or subcontracted) to a rate of zero, especially accidents that could result in lost work time, different levels of disability, or even fatalities. Facility rates may be benchmarked against the performance of facilities in this sector in developed countries through consultation with published sources (e.g. US Bureau of Labor Statistics and UK Health and Safety Executive)[30].

Occupational Health and Safety Monitoring

The working environment should be monitored for occupational hazards relevant to the specific project. Monitoring should be

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[26] Available at: http://www.acgih.org/TLV/

[27] Available at: http://www.cdc.gov/niosh/npg/

[28] Available at: http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9992

[29] Available at: http://europe.osha.eu.int/good_practice/risks/ds/oel/

[30] Available at: http://www.bls.gov/iif/ and http://www.hse.gov.uk/statistics/index.htm

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designed and implemented by accredited professionals [31] as part

of an occupational health and safety monitoring program.

Facilities should also maintain a record of occupational

accidents and diseases and dangerous occurrences and

accidents. Additional guidance on occupational health and

safety monitoring programs is provided in the **General EHS**

Guidelines.

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[31] Accredited professionals may include Certified Industrial Hygienists,
Registered Occupational Hygienists, or Certified Safety Professionals or their
equivalent.

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3.0   References

Australian Government, Department of the Environment and Heritage. 2004. Emission Estimation Technique Manual for Inorganic Chemicals Manufacturing. Version 2.0. Canberra, Australia

European Integrated Pollution Prevention and Control Bureau (EIPPCB). 2001. Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing Industry. December 2001. Sevilla, Spain

EIPPCB. 2006a. Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in Large Volume Inorganic Chemicals - Solids and Others Industry. October 2006. Sevilla, Spain

EIPPCB. 2006b. Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers. December 2006. Sevilla, Spain

European Fertilizer Manufacturers Association (EFMA). 2000a. Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry. "Production of Ammonia," Booklet No. 1. Brussels, Belgium

EFMA. 2000b. Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry. "Production of Nitric Acid," Booklet No. 2. Brussels, Belgium

EFMA. 2000c. Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry. "Production of Sulphuric Acid," Booklet No. 3. Brussels, Belgium

EFMA. 2000d. Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry. "Production of Phosphoric Acid," Booklet No. 4. Brussels, Belgium

German Federal Government. 2002. First General Administrative Regulation Pertaining the Federal Immission Control Act (Technical Instructions on Air Quality Control – TA Luft). Berlin, Germany

German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety. 2004. Promulgation of the New Version of the Ordinance on Requirements for the Discharge of Waste Water into Waters (Waste Water Ordinance - AbwV) of 17. June 2004. Berlin, Germany

Helsinki Commission. 2002. Helcom Recommendation 23/6. Reduction of Emissions and Discharges of Mercury from Chloralkali Industry. Helsinki, Finland.

Intergovernmental Panel on Climate Change (IPCC). 2006. Special Report, Carbon Dioxide Capture and Storage, March 2006. Geneva, Switzerland

Kirk-Othmer, R.E. 2006. Encyclopedia of Chemical Technology. 5th Edition. John Wiley and Sons Ltd., New York, NY

National Fire Protection Association (NFPA). 2000. Standard 850: Recommended Practice for Fire Protection for Electric Generating Plants and High Voltage Direct Current Converter Stations. 2000 Edition. Quincy, Massachusetts

NFPA. 2004. Standard 120: Standard for Fire Prevention and Control in Coal Mines. 2004 Edition. Quincy, Massachusetts

Paris Commission. 1990. Parcom Decision 90/3 of 14 June 1990 on Reducing Atmospheric Emissions from Existing Chlor-Alkali Plants. Paris, France

UK Environmental Agency. 1999a. IPC Guidance Note Series 2 (S2) Chemical Industry Sector. S2 4.03: Inorganic Acids and Halogens. Bristol, UK

UK Environmental Agency. 1999b. IPC Guidance Note Series 2 (S2) Chemical Industry Sector. S2 4.04: Inorganic Chemicals. Bristol, UK

UK Environmental Agency. 2004a. Sector Guidance Note IPPC S4.03. Guidance for the Inorganic Chemicals Sector. Bristol, UK

UK Environmental Agency. 2004b. Process Guidance Note 6/42 (04). Secretary of State's Guidance for Bitumen and Tar Processes. Bristol, UK

US Environmental Protection Agency (EPA). Office of Compliance. 1995. Sector Notebook Project. Profile of the Inorganic Chemical Industry. Washington, DC

US EPA. 40 CFR Part 60, Standards of Performance for New and Existing Stationary Sources: Subpart G—Standards of Performance for Nitric Acid Plants. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 60, Standards of Performance for New and Existing Stationary Sources: Subpart H—Standards of Performance for Sulfuric Acid Plants. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 60, Standards of Performance for New and Existing Stationary Sources: Subpart T—Standards of Performance for the Phosphate Fertilizer Industry: Wet-Process Phosphoric Acid Plants. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 63, National Emission Standards for Hazardous Air Pollutants for Source Categories: Subpart AA—National Emission Standards for Hazardous Air Pollutants From Phosphoric Acid Manufacturing Plants. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 63, National Emission Standards for Hazardous Air Pollutants for Source Categories: Subpart IIIII—National Emission Standards for Hazardous Air Pollutants: Mercury Emissions From Mercury Cell Chlor-Alkali Plants. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 63, National Emission Standards for Hazardous Air Pollutants for Source Categories: Subpart NNNNN—National Emission Standards for Hazardous Air Pollutants: Hydrochloric Acid Production.

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Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html
(accessed on October 2006)

US EPA. 40 CFR Part 414. Subpart G—Bulk Organic Chemicals. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 414. Subpart I—Direct Discharge Point Sources That Use End-of-Pipe Biological Treatment. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 414. Subpart J—Direct Discharge Point Sources That Do Not Use End-of-Pipe Biological Treatment. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 415. Subpart F—Chlor-alkali Subcategory (Chlorine and Sodium or Potassium Hydroxide Production). Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 415. Subpart H—Hydrofluoric Acid Production Subcategory. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 418. Subpart A—Phosphate Subcategory. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 418. Subpart B—Ammonia Subcategory. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 418. Subpart E—Nitric Acid Subcategory. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 422. Subpart D—Defluorinated Phosphate Rock Subcategory. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 422. Subpart E—Defluorinated Phosphoric Acid Subcategory. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

US EPA. 40 CFR Part 458. Subpart A—Carbon Black Furnace Process Subcategory. Washington, DC. Available at http://www.gpoaccess.gov/cfr/index.html (accessed on October 2006)

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Annex A: General Description of Industry Activities

This EHS Guideline for Large Volume Inorganic Compound (LVIC) Manufacturing and Coal Tar Distillation includes Ammonia; Chlor-Alkali (i.e., chlorine, caustic soda, soda ash, etc.); Acids (Nitric, Hydrochlodric, Sulfuric, Hydrofluodric, Phosphoric); Carbon Black; and Coal Tar Distillation (naphthalene, phenanthrene, anthracene) sectors. It covers the production of major intermediates and products for the downstream industry covering many diversified sectors ranging from fertilizers to plastics. It is characterized by large volume productions, which can reach up to million ton per year and be manufactured in large facilities.

Ammonia [32]

About 80 % of ammonia (NH_3) is currently used as the nitrogen source in fertilizers, with the remaining 20 % applied in several industrial applications, such as the manufacture of plastics, fibres, explosives, hydrazine, amines, amides, nitriles and other organic nitrogen compounds which serve as intermediates in dyes and pharmaceuticals manufacturing. Important inorganic products manufactured from ammonia include nitric acid, urea and sodium cyanide. Liquid ammonia is an important solvent and is also used as a refrigerant.

Ammonia plants may be built as stand-alone or integrated with other plants at a site, typically with urea production. However recent trends include combined ammonia with methanol production. Hydrogen and / or carbon monoxide production can also be integrated with ammonia plants. An ammonia plant typically produces around 2,000 tonnes per day, but plants that can produce up to 3,400 tonnes per day have been built.

The natural gas reforming with steam and air is the simplest and most efficient way of ammonia synthesis gas production and is today the most used.

Ammonia is produced by an exothermic reaction of hydrogen and nitrogen. This reaction is carried out in the presence of metal oxide catalysts at elevated pressure. Catalysts used in the process may contain cobalt, molybdenum, nickel, iron oxide / chromium oxide, copper oxide / zinc oxide, and iron. The ammonia product, in liquefied form, is stored either in large atmospheric tanks at temperature of −33 degrees centigrade or in large spheres at pressures up to 20 atmospheres at ambient temperature. The raw material source of nitrogen is atmospheric air and it may be used in its natural state as compressed air or as pure nitrogen from an air liquefaction plant. Hydrogen is available from a variety of sources such as natural gas, crude oil, naphtha, or off gases from processes such as coke oven or refineries.

Ammonia production from natural gas includes the following process steps: removal of trace quantities of sulfur in the feedstock; primary and secondary reforming; carbon monoxide shift conversion, removal of carbon dioxide, methanation, compression, ammonia synthesis, and ammonia product refrigeration. Carbon is removed in the form of concentrated CO_2, which should preferably be used for urea manufacture or other industrial purposes to reduce its release to the atmosphere.

Two other non conventional process routes include: (1) the addition of extra process air to the secondary reformer with cryogenic removal of the excess nitrogen, and (2) heat-exchange autothermal reforming. The second process route has

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[32] EIPPCB. 2006b; EFMA. 2000a

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some environmental advantage because of the reduced need for firing in the primary reformer and the potential to lower energy consumption. It is a recent technology and, to date, built for a capacity of about 500 tonnes NH_3 per day.

Liquefied ammonia from production plants is either used directly in downstream plants or transferred to storage tanks. From storage the ammonia can be shipped to users, through road tankers, rail tank cars or ships. Ammonia is usually stored by using one or other of three methods:

- Fully refrigerated storage in large tanks with a typical capacity of 10,000 to 30,000 tonnes (up to 50,000)

- Pressurized storage spheres or cylinders with a capacity up to about 1,700 tonnes

- Semi-refrigerated tanks.

There are several storage types for refrigerated liquid products. The most important types are:

- Single containment: a single-wall insulated tank, usually with a containment bund around it;

- Double containment: tanks with two vertical walls, both designed to contain the stored liquid and withstand its hydrostatic pressure. The roof rests on the inner wall; and

- Full containment: closed storage tanks with two walls, as for double containment, but with the roof resting on the outer wall and using an adequate margin between operating and relief pressure.

Nitric Acid[33]

The production stages for nitric acid manufacture include the following: vaporizing liquid ammonia; mixing the vapor with air

and burning the mixture over a platinum/rhodium catalyst; cooling the resultant nitric oxide (NO) and oxidizing it to nitrogen dioxide (NO_2) with residual oxygen; and absorbing the nitrogen dioxide in water in an absorption column to react into nitric acid. Large-capacity plants normally have dual-pressure design (e.g. medium-pressure combustion and high-pressure absorption), while small plants may have combustion and absorption conducted at the same pressure. High pressure in the absorption column reduces the nitrogen oxides (NO_X) emissions. Generation of NO_X and nitrous oxide (N_2O), which is a greenhouse gas, in nitric acid plants is significant; however catalytc conversion techniques can reduce the emission level by more than 80 percent.

The recommended material for tanks, vessels and accessories is low carbon austenitic stainless steel. Transfer to transport vessels is typically via pumping or by gravity. Pressurizing for unloading large quantities should be avoided. Nitric acid is transported using rail tank cars, road tankers and less frequently, ships.

The typical capacity of modern plants for producing nitric acid is approximately 1,000 tons per day.

Sulfuric Acid[34]

The most important use of sulfuric acid (H_2SO_4) is in the phosphate fertilizer industry. Sulfuric acid is manufactured from sulfur dioxide (SO_2) produced by combustion of elemental sulfur. Liquid sulfur is a product of the desulfurization of natural gas or the cleaning of coal flue-gas; another possible route is the melting of naturally occurring solid sulfur. Sulfur dioxide is also produced by the metals industry, through roasting and smelting processes generating off-gases with a sufficiently high

[33] EIPPCB. 2006b; EFMA. 2000b.

[34] EIPPCB. 2006b; EFMA. 2000c.

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concentration of SO_2 to allow direct processing to H_2SO_4. The thermal oxidizing process of spent acids used as raw materials is another route to produce SO_2 and H_2SO_4. The exothermic oxidation of sulfur dioxide over several layers of a suitable catalyst (i.e., vanadium pentoxide) to produce sulfur trioxide (SO_3) is the process used today in almost all sulfuric acid manufacturing plants. Modern plants can be designed to be very efficient in terms of sulfur dioxide conversion (more than 99%) and energy recovery.

Sulfuric acid is obtained from the absorption of SO_3 and water into H_2SO_4 (with a concentration of at least 98%). SO_3 is absorbed in an intermediate absorber installed after the second or third catalyst layer in a double contact process, where the gases are then conveyed to the final catalyst layer(s) and the SO_3 formed here is absorbed in a final absorber. The final absorber is installed after the last catalyst layer in a single contact process. The warm acid produced is sparged with air in a column or in a tower to collect the remaining SO_2 in the acid; the SO_2 laden air is returned to the process.

Phosphoric Acid[35]

Phosphoric acid (H_3PO_4) is primarily used in the manufacture of phosphate salts (fertilizers and animal feed supplements). Two different processes can be used in the manufacture of phosphoric acid. In the first process, known as the thermal process, elemental phosphorus is produced from phosphate rock, coke and silica in an electrical resistance furnace and is then oxidized and hydrated to form the acid. Thermal-generated acid is considerably pure, but also expensive, and hence produced in small quantities, mainly for the manufacture of industrial phosphates.

The second types of processes, known as wet processes, are those digesting phosphate rocks with an acid (i.e. sulfuric, nitric or hydrochloric acid). The wet digestion of phosphate rock with sulfuric acid is the preferred process in term of volume. The tri-calcium phosphate from the phosphate rock reacts with concentrated sulfuric acid to produce phosphoric acid and calcium sulfate that is an insoluble salt. The operating conditions are generally selected so that the calcium sulfate is precipitated as the dihydrate (DH) or hemihydrate (HH) form.

The main production steps are the following: grinding of phosphate rock; reaction with sulfuric acid in a series of separate agitated reactors at a temperature of 70-80 °C; and filtration to separate the phosphoric acid from the calcium sulfate.

Phosphoric acid is most commonly stored in rubber-lined steel tanks, although stainless steel, polyester and polyethylene-lined concrete are also used. Storage tanks are normally equipped with some means of keeping the solids in suspension to avoid costly cleaning of the tank.

Hydrofluoric Acid[36]

Hydrogen fluoride (HF) is produced in two forms, as anhydrous hydrogen fluoride and as aqueous hydrofluoric acid. The predominant form manufactured is hydrogen fluoride, a colorless liquid or gas that fumes when in contact with air and is water-soluble. Hydrogen fluoride is also a fortuitous by-product in the manufacture of superphosphate fertilizers. Hydrofluoric acid is used in glass etching and polishing, petroleum alkylation, and stainless steel pickling. Hydrofluoric acid is also used to produce fluorocarbons for the manufacture of resins, solvents, stain removers, surfactants, and pharmaceuticals.

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[35] EIPPCB. 2006b; EFMA. 2000d

[36] EIPPCB. 2006b

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Hydrofluoric acid is manufactured by the reaction of acid-grade fluorspar (CaF_2) with sulfuric acid (H_2SO_4). The endothermic reaction is conducted in horizontal rotary kilns externally heated to 200 to 250°C. Dry fluorspar and a slight excess of sulfuric acid are fed continuously to the front end of a stationary pre-reactor for mixing or directly to the kiln by a screw conveyor. Calcium sulfate ($CaSO_4$) is removed through an air lock at the opposite end of the kiln.

The gaseous reaction products - hydrogen fluoride and excess H_2SO_4 from the primary reaction, and silicon tetrafluoride (SiF_4), sulfur dioxide (SO_2), carbon dioxide (CO_2), and water vapor produced in secondary reactions - are removed from the front end of the kiln along with entrained particulate matter. The particulate matter is then removed from the gas stream and returned to the kiln. Sulfuric acid and water are removed in a pre-condenser. Hydrogen fluoride vapors are subsequently condensed in refrigerant condensers forming crude HF, which is sent to intermediate storage tanks. The remaining gas stream passes through a sulfuric acid absorption tower or acid scrubber, removing most of the remaining hydrogen fluoride and some residual sulfuric acid, which are also sent to intermediate storage. The gases exiting the acid scrubber are treated in water scrubbers, where both SiF_4 and remaining HF are recovered as hexafluorosilicic acid (H_2SiF_6). The water scrubber tail-gases are passed through a caustic scrubber before being emitted to the atmosphere. The hydrogen fluoride and sulfuric acid are delivered from intermediate storage tanks to distillation columns, where the hydrofluoric acid is extracted at 99.98 percent purity. A final dilution step with water is needed to produce weaker concentrations (typically 70 to 80 percent).

Anhydrous HF is a liquid which boils at 19.5 °C. The liquid HF is kept at low temperature, preferably below 15 °C, by cooling or by the installation of condensers in vent storage pipelines which

condense the evaporating HF. Liquid HF is normally stored at atmospheric pressure in carbon steel tanks, where a thin protective layer of FeF_2 is formed, preventing the tank walls from further corrosion. Liquid velocity in the pipelines should be below 1 m/s to avoid erosion of the FeF_2 layer. Hydrofluoric acid with a concentration of at least 70 % is also stored in carbon steel tanks, whereas acid with concentrations of less than 70 % is stored in lined steel tanks or alternatively in polyethylene tanks.

Hydrochloric Acid[37]

Hydrochloric acid (HCl) is a versatile chemical used in a variety of chemical processes, including hydrometallurgical processing, chlorine dioxide syntheses, hydrogen production, and miscellaneous cleaning and etching operations. It is also a common ingredient in many chemical reactions, and a commonly used acid for catalyzing organic processes.

The acid is manufactured by several different processes. commonly applied production processes consist of reacting sodium chloride with sulfuric acid, or more recently, the acid is generated as a by-product of the chlorination reaction process (e.g., production of chlorinated solvents and organics).

Chlor-alkali[38]

The chlor-alkali industry produces chlorine (Cl_2) and alkali (i.e., caustic soda or sodium hydroxide (NaOH) and potassium hydroxide (KOH)), by electrolysis of a salt solution, mainly using sodium chloride (NaCl) as feed or potassium chloride (KCl) for the production of potassium hydroxide. The chlor-alkali process is an important consumer of electrical energy.

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[37] Australian Government, Department of the Environment and Heritage. 2004.
[38] EIPPCB. 2001.

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The main chlor-alkali manufacturing technologies are mercury, diaphragm and membrane cell electrolysis. In the chlorine process, chlorine gas leaving the electrolyzers is at approximately 80-90 ºC and saturated with water vapor. It also contains impurities such as brine mist, nitrogen, hydrogen, oxygen, carbon dioxide and traces of chlorinated hydrocarbons. After direct or indirect cooling and impurities removal, chlorine is passed to the drying towers for drying with concentrated sulfuric acid. The gas is then compressed and liquefied at different pressure and temperature levels. Liquefied chlorine is stored in bulk tanks at ambient or low temperature.

The membrane cell process has environmental advantages over the two older processes, in addition to be currently the most economically advantageous process. The anode and cathode are separated by a water-impermeable ion-conducting membrane. Brine solution flows through the anode compartment where chloride ions are oxidized to chlorine gas. The sodium ions migrate through the membrane to the cathode compartment which contains caustic soda solution. The demineralized water added to the catholyte circuit is hydrolyzed, and releases hydrogen gas and hydroxide ions. The sodium and hydroxide ions combine to produce caustic soda which is typically brought to a concentration of 32-35% by recirculating the solution before discharge from the cell. Higher concentrations are produced concentrating the caustic liquor by steam evaporation. The output of caustic soda is proportional to that of chlorine (1.128 tonnes of caustic soda (100%) are produced by electrolysis per tonne of chlorine). Because of the membrane, the caustic soda solution contain a very limited amount of salt due to migration of chloride, as in the diaphragm cell process. Depleted brine is discharged from the anode compartment and resaturated with salt.

The cathode material used in membrane cells is either stainless steel or nickel and the anodes used are metal. The cathodes are often coated with a catalyst that increases surface area and reduces over-voltage. Coating materials include Ni-S, Ni-Al, and Ni-NiO mixtures, as well as mixtures of nickel and platinum group metals. The membranes used in the chlor-alkali industry are commonly made of perfluorinated polymers.

Chlorine is often produced near consumers. Storage and transport of chlorine requires proper handling and use of best practice to minimize potential hazards. Chlorine is transported by pipe, road and rail.

Hydrogen is a co-product of the electrolysis of brine (28 kg for 1 tonne of chlorine) and is generally used on-site as a combustible, sent as a fuel to other companies, or sold and transported as chemical. It can be used on integrated sites for certain applications because of its high purity, including synthesis of ammonia, methanol, hydrochloric acid, hydrogen peroxide, etc.

In addition to cell electrolysis, there are processing steps which are common to all technologies and include: salt unloading and storage, brine purification and resaturation, chlorine, caustic soda, and hydrogen processing.

The brine purification process consists of a primary system for the mercury and diaphragm technologies and an additional secondary system for membrane technology. This operation is needed to eliminate impurities (sulfate anions, cations of calcium, magnesium, barium and metals) that can affect the electrolytic process.

The primary brine purification uses sodium carbonate and sodium hydroxide to precipitate calcium and magnesium ions as calcium carbonate ($CaCO_3$) and magnesium hydroxide

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$(Mg(OH)_2)$. Metals may also precipitate as hydroxide during this operation. Sodium sulfate may be controlled by adding calcium chloride $(CaCl_2)$ or barium salts (which however may represent a hazard due to their toxicity) to remove sulfate anions by precipitation of calcium sulfate $(CaSO_4)$ or barium sulfate $(BaSO_4)$. After precipitation, impurities are removed by sedimentation, filtration or a combination of both. Other possibilities to remove sulfates include ultra-filtration and brine purging.

The secondary brine purification consists of a polish filtration step and brine softening in an ion exchange unit generally with filters in order to sufficiently reduce the suspension matter and protect the ion-exchange resin from damage. The ion exchange chelating resin treatment is designed to decrease the alkaline earth metals to trace levels. The resin is periodically regenerated with high purity hydrochloric acid and sodium hydroxide solutions.

Instead of diluting the remaining gases after partial condensation of the chlorine gas, the hydrogen is removed by means of a reaction with chlorine gas in a column. This step produces gaseous hydrochloric acid, which can be recovered in a hydrochloric acid unit.

Soda Ash[39]

Sodium carbonate (Na_2CO_3) or soda ash is a fundamental raw material to the glass, soaps and detergents, and chemicals industries. Soda ash (calcined soda) is manufactured in two grades: 'light soda ash' and 'dense soda ash'. Dense soda ash is mainly used in the glass industry and for economic transportation over long distances. The light form is used mainly for the detergent market and certain chemical intermediates.

Soda ash is generally manufactured by large, highly integrated production units, with a plant capacity ranging from 150 to 1,200 kt per year.

The Solvay process (ammonia soda process) involves saturation of brine with ammonia and carbon dioxide gas. The process uses salt brine (NaCl) and limestone $(CaCO_3)$ as raw materials. Ammonia is almost totally regenerated and recycled. The main advantage of this process is the widespread availability of the relatively pure raw materials, which allow operating production units relatively close to the market.

The Solvay process produces 'light soda ash', with a pouring density of about 500 kg/m^3. 'Light soda ash' is transformed by recrystallization first to sodium carbonate monohydrate, and then to 'dense soda ash' after drying (dehydration). Dense soda ash has a pouring density of about 1,000 kg/m^3. Dense soda ash can also be produced by compaction.

Carbon Black[40]

Carbon black is produced by partial oxidation or thermal decomposition of hydrocarbons. About 65 – 70 % of the world's consumption of carbon black is used in the production of tires and tire products for automobiles and other vehicles. Roughly 25 - 30% is used for other rubber products and a small percent is used in plastics, printing ink, paint, paper and miscellaneous applications.

Carbon black differs from other carbon-based materials in many respects, especially in bulk density. Mixtures of gaseous or liquid hydrocarbons represent the raw materials preferable for industrial production with preference to aromatic hydrocarbons for better yields.

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[39] EIPPCB. 2006a.

[40] EIPPCB. 2006a.

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The processes are divided into two groups: those employing incomplete or partial combustion and those based on thermal cracking. In the partial combustion processes, air is used to burn part of the feedstock, producing the energy required to carry out the pyrolysis, whereas in the thermal cracking process, heat is generated externally and introduced into the process.

The furnace black process is currently the most important production process. It accounts for more than 95% of the total worldwide production. It is a continuous process and its advantages are its great flexibility and its better economy compared to other process. The typical production rate is approximately 2,000 kg/h for a modern furnace black reactor. In furnace black, a heavy aromatic feedstock is injected by atomization into a high speed stream of combustion gases and partially burned and mostly cracked (45 – 65%) to produce carbon black and hydrogen at a temperature ranging from 1200 to 1700° C. After quenching with water, carbon black is recovered by cyclones and bag filters, pellettized, dried and delivered to storage (silos) or shipped.

Coal Tar Distillation

Coal tar is currently almost totally distilled mainly in continuous stills that have daily capacities of 100–700 tons. It is a condensation product obtained by cooling the gas evolved in coal distillation (pyrolysis or carbonization of coal). Coal tar is a black viscous liquid denser than water. Coal-tar pitch is a black very viscous, semisolid, or solid residue from the distillation of coal tar.

The coal tar product, which distills up to about 400°C at atmospheric pressure, is primarily a complex mixture of mono- and polycyclic aromatic hydrocarbons, a proportion of which are substituted with alkyl, hydroxyl, amine and/or hydro sulfide

groups, and to a lesser extent their sulfur-, nitrogen-, and oxygen-containing analogues. Tars produced at the lower coal carbonization temperatures also contain hydroaromatics, alkanes, and alkenes. The residue from the distillation is at least 50% of the coal tar products by high temperature carbonization and consists of a continuation of the sequence of polynuclear aromatic, aromatic, and heterocyclic compounds, up to molecules containing 20 to 30 rings.

Metal corrosion associated to continuous coal tar distillation is a typical issue to be considered in plant management. The ammonium salts (mainly ammonium chloride), associated with the entrained liquor remain in the tar after dehydration, tend to dissociate with the production of hydrochloric acid. This acid may deteriorate any equipment parts in which these vapors and steam are present above 240°C, including the condensers on the dehydration and fractionation columns. Corrosion is controlled by the addition of alkali (either sodium carbonate solution or caustic soda) to the tar.

A primary distillation product pattern at a tar-processing plant can give only one fraction, naphthalene oil taken between 180 and 240°C, or two fractions, light creosote or middle oil (230–300°C) and heavy creosote or heavy oil (above 300°C) between the naphthalene oil and pitch.

The higher boiling cresylic acids are mixtures of cresols or xylenols with higher boiling phenols. Their main uses are in phenol-formaldehyde resins, solvents for wire-coating enamels, metal degreasing agents, froth-flotation agents, and synthetic tanning agents.

Naphthalene is the principal component of coke-oven tars and the only component that can be concentrated to a reasonably

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high content on primary distillation[41]. Naphthalene oils can be further upgraded by several methods, mainly based on crystallization of the primary naphthalene oil to upgrade to phthalic grade quality or to convert the latter into the purer chemical grade anthracene oils. Naphthalene has been traditionally used for the production of phthalic anhydride, ß-naphthol and dye stuff intermediates. More recently, naphthalene has been used in condensation products from naphthalene sulfonic acids, utilizing formaldehyde as additives to improve the flow properties of concrete. Another application is the production of diisopropylnaphthalenes.

Crude anthracene is isolated from coke-oven anthracene oils. Where the anthracene oil gives only a limited residue at 360°C, the oil is diluted using naphthalene drained oil or a light wash oil and this blend is cooled to 35°C. The resulting solid–liquid slurry is filtered or centrifuged to give a crude anthracene oil containing 40–45% anthracene.

The recovery of tar chemicals leaves residual oils, including heavy naphtha, dephenolated carbolic oil, naphthalene drained oil, wash oil, strained anthracene oil, and heavy oil. These are blended to give creosote oils, which have been used as timber preservatives Coal-tar creosote is also a feedstock for carbon black manufacture. Other smaller markets for creosote are for fluxing coal tar, pitch, and bitumen.

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[41] Naphthalene oils from coke-oven tars generally contain 60–65% of naphthalene.