

CLEANING OF EQUIPMENT

DEP 70.10.80.11-Gen.

January 1998
(DEP Circular 42/04 has been incorporated)

DESIGN AND ENGINEERING PRACTICE



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1. INTRODUCTION

1.1 SCOPE

This DEP specifies requirements and gives recommendations for chemical and mechanical cleaning methods for the removal of fouling deposits, including practical cleaning methods for various types of equipment, and a brief description of sludge removal from crude oil storage tanks.

This DEP is a revision of the DEP of the same number dated September 1992.

Excluded from the scope of this DEP is the cleaning or drying of transmission pipelines.

1.2 DISTRIBUTION, INTENDED USE AND REGULATORY CONSIDERATIONS

Unless otherwise authorised by SIOP and SIEP, the distribution of this DEP is confined to companies forming part of the Royal Dutch/Shell Group or managed by a Group company, and to Contractors nominated by them (i.e. the distribution code is "C", as defined in DEP 00.00.05.05-Gen.).

This DEP is intended for use in oil refineries, supply/marketing installations, chemical plants, gas plants, and, where applicable, in exploration and production facilities.

If national and/or local regulations exist in which some of the requirements may be more stringent than in this DEP the Contractor shall determine by careful scrutiny which of the requirements are the more stringent and which combination of requirements will be acceptable as regards safety, environmental, economic and legal aspects. In all cases the Contractor shall inform the Principal of any deviation from the requirements of this DEP which is considered to be necessary in order to comply with national and/or local regulations. The Principal may then negotiate with the Authorities concerned with the object of obtaining agreement to follow this DEP as closely as possible.

1.3 DEFINITIONS

The **Contractor** is the party which carries out all or part of the design, engineering, procurement, construction, commissioning or management of a project, or operation or maintenance of a facility. The Principal may undertake all or part of the duties of the Contractor.

The **Manufacturer/Supplier** is the party which manufactures or supplies equipment and services to perform the duties specified by the Contractor.

The **Principal** is the party which initiates the project and ultimately pays for its design and construction. The Principal will generally specify the technical requirements. The Principal may also include an agent or consultant authorised to act for, and on behalf of, the Principal.

The word **shall** indicates a requirement.

The word **should** indicates a recommendation.

1.4 CROSS-REFERENCES

Where cross-references to other parts of this DEP are made, the referenced section number is shown in brackets. Other documents referenced by this DEP are listed in (8).

2. FOULING

Inorganic scales, corrosion products, dirt, sand, organic growth and organic sediments are all common sources of fouling.

Fouling deposits range from very tenacious scales to thick layers of deposits of varying hardness. These layers are categorised as general fouling when contaminants in the form of small suspended particles are deposited on the surface. The settling rate is directly proportional to particle size and inversely proportional to liquid viscosity and density. These deposits are normally soft and easy to remove; a common form of general fouling is sludge.

Scaling is generally caused by precipitation of solids (salts) out of solution onto heat exchange surfaces, due to high concentrations or increased temperature. Scaling can also be caused by sulphide or oxide layers formed by high temperature corrosion.

Fouling has a negative effect on the performance of equipment. The type and content of fouling or deposit formation is related to the process or type of equipment. Common signs of fouling are flow reduction, increased pressure drop, reduced heat transfer or under deposit corrosion. Visual inspection, radiography or thermography may also indicate the extent of fouling.

Although equipment may be designed to minimise fouling, the possibility of fouling can never be entirely eliminated. Chemical and mechanical cleaning methods will normally be required and the necessary provisions should be made.

Fouling deposits can be divided into several types:

2.1 INORGANIC DEPOSITS

These can form in heat transfer equipment (usually on the cooling water side), inside boiler tubes and on external surfaces of boiler and furnace tubes. These scales/deposits may be formed by combustion of fuels, by corrosion of the equipment or, in heat transfer equipment, by precipitation from the water stream or process stream at elevated temperatures. The deposits mainly consist of one or more of the following components:

- carbonates, oxides or hydroxides of calcium, magnesium, iron, manganese, copper and zinc;
- phosphates of calcium, magnesium and iron;
- sulphides of iron, copper, zinc and ammonium;
- sulphates of calcium;
- chlorides of calcium, magnesium, ammonium and sodium;
- vanadium pentoxide;
- silica/silicates;
- fluorides.

2.2 ORGANIC DEPOSITS

Organic fouling formed by biological growth such as slime, algae, shellfish, jellyfish and barnacles are encountered in cooling water circuits. On the process side of equipment, organic deposits (varying from light hydrocarbons to heavy polymers) and coke may be found, depending on the composition and temperature of the process stream.

2.3 MIXED INORGANIC/ORGANIC DEPOSITS

A mixture of inorganic/organic fouling is sometimes encountered in water circuits, when hydrocarbons and/or chemical products leak from the process side.

2.4 POLYTHIONIC ACID STRESS CORROSION CRACKING

CAUTION:

In H₂S service, a neutralisation procedure shall be applied prior to opening any equipment containing austenitic stainless steel components (e.g. HDS reactors) in order to protect against polythionic acid stress corrosion cracking. Details of the procedure can be found in NACE RP0170.

3. CHEMICAL CLEANING

3.1 GENERAL

Chemical cleaning is the process of removing fouling deposits with chemical solutions. The cleaning action may be entirely chemical, using acids or caustics, but may also be assisted by physical means using solvents, steam or hot water.

Cleaning operations shall be conducted in such a way that they will not lead to unacceptable pollution of the environment.

Most inorganic deposits can be removed by using acids or acid-based commercial cleaning agents, while alkaline solutions can be used for the removal of some organic deposits. Mixtures of cleaning solutions, such as high-aromatic solvents (excluding benzene) with an emulsifying agent, may remove some tar and polymer deposits.

To determine the most suitable cleaning agent for a particular application, a representative sample of the fouling deposit shall be investigated in a laboratory. The envisaged cleaning agent and corrosion inhibitor shall be tested on the sample at the same temperature that will be used for the actual cleaning process. If sample deposits cannot be obtained then the experience of the contractor and/or other Shell Operating Units should be requested.

Cleaning procedures should be available before plant or equipment is shut down and based on deposit samples taken on some previous occasion. The procedure and frequency of cleaning should be noted in a "plant cleaning manual" or similar document and should be reviewed periodically to identify areas of improvement.

For equipment that cannot be moved and for systems of vessels and piping, etc., chemical cleaning can be carried out in situ, using mobile facilities to circulate cleaning agents through the equipment.

Chemical cleaning can also be carried out by immersion of equipment in a cleaning agent. This is suitable for small parts or for equipment containing deposits difficult to remove in situ, such as plugged heat exchangers. The immersion procedure should be carried out in a central cleaning yard. Sometimes an additional cleaning method, such as high pressure (HP) water jetting, is required after immersion.

On-stream chemical cleaning should be applied only after careful consideration since process temperatures may not be suitable and contamination by the cleaning agent could occur throughout the system (see 3.4.7 and 3.4.8).

Chemical cleaning should be carried out by specialised contractors unless the Principal has sufficiently experienced labour. Before a contract is awarded, adequate arrangements shall be made for neutralisation and environmentally acceptable disposal of used cleaning agents. The Contractor's equipment and procedures shall be approved by the Principal before the work starts. The Principal's focal point shall monitor that the work is carried out in accordance with the approved procedure, that all safety precautions are taken and that used cleaning agents are disposed of in an environmentally acceptable way.

Before starting any unproven chemical cleaning activity, the following basic rules shall be complied with (see 3.6.1):

- a corrosion test shall be carried out on an inhibited acid sample, using test coupons of the metals of the equipment or systems to be cleaned. Some fouling deposit shall also be added as this may influence the attack on the test strips;
- to monitor corrosion, coupons or probes should be installed in the equipment or system prior to the cleaning activity;
- the equipment shall be inspected before and after cleaning to check the effectiveness of the cleaning operation and to look for signs of metal attack (welds may be more vulnerable);
- prior to the introduction of chemicals, a hydrostatic test of the entire system should be performed at the system design test pressure to check for leakage. This shall be repeated after all cleaning operations are completed.

3.2 SURFACTANTS

Surfactant solutions are becoming more widely used to improve the effectiveness and reduce the time needed for equipment decontamination during process unit shutdowns. The primary objective of the decontamination phase of a shutdown is the removal of hazardous materials from vessels, piping, and auxiliary equipment. However, surfactants can also effectively clean refinery equipment by eliminating residual bulk hydrocarbons, as well as hydrocarbon films and sludges.

Typically, commercially available surfactants specifically designed for the petrochemical industry are mixed with circulating hot water at a temperature of between 80 °C and 90 °C. A surfactant concentration of between 1% and 2% is usually employed depending on the nature of the hydrocarbon to be removed. The surfactant causes an emulsion to form between the hydrocarbon and the water phases. The emulsion is removed to a holding tank where the emulsion is broken, usually adding a salt solution; typically calcium chloride. The hydrocarbon phase can then be recovered and processed. The water phase is usually removed through the site water treating facilities.

Experience has shown that surfactant cleaning can reduce the time required during shutdowns by 50% or more. The time saved and the resultant increase in plant availability can often more than offset the costs of surfactant cleaning. Details of some experience can be found in articles 10, 11 and 12 of the SIOP Maintenance and Inspection Bulletin, 16th edition (December 1996).

3.3 ADVANTAGES AND LIMITATIONS OF CHEMICAL CLEANING

When compared with mechanical cleaning, chemical cleaning has advantages and limitations as follows:

The advantages of chemical cleaning are:

- cleaning can often be carried out without dismantling the equipment;
- cleaning is more effective since all parts (assuming no blockages) will be reached, resulting in more uniform cleaning;
- when carried out by competent personnel, the damage caused by chemical cleaning is generally less than that due to conventional mechanical cleaning. Any damage induced by conventional mechanical cleaning could enhance corrosion and/or fouling during subsequent operation.

The limitations of chemical cleaning are:

- chemically inert material, e.g. coke deposits, cannot be removed;
- severely fouled or fully plugged equipment will require mechanical cleaning since the circulation of cleaning agents would be impossible, or so limited as to render chemical cleaning ineffective;
- corrosion rates of materials during chemical cleaning are generally low, but severe damage may still occur if improper procedures are applied, e.g. stress corrosion cracking of stainless steel induced by chlorides, stress corrosion cracking of carbon steel (and other metals) caused by hydrogen sulphide released during chemical cleaning, caustic embrittlement of carbon steel and risk of hydrogen induced cracking (HIC)/blistering because sulphide-containing scale is present;
- safe and environmentally acceptable disposal of cleaning agents is required after neutralisation;
- emissions released during cleaning may have to be treated to protect all personnel in the area as well as the environment.

Combination of chemical and mechanical cleaning:

- In some cases where tenacious deposits such as residues are present chemical cleaning using surfactants, followed by mechanical cleaning (H.P water jetting), may be the most effective.

3.4 CLEANING AGENTS

For chemical/physical cleaning a selection should be made from the following agents:

Note: Oil and grease shall be removed prior to any acid cleaning to ensure that the acids come into contact with the deposits. An alkaline wash is recommended.

3.4.1 Hydrochloric acid

This acid is mostly used in cleaning because it is relatively cheap and usually readily available. It effectively removes many inorganic deposits containing e.g. carbonates and iron sulphide. Because it is very corrosive towards most metals, effective inhibitors shall be used which will reduce corrosion without affecting the cleaning action.

Hydrochloric acid is typically applied in a concentration of 2% to 5% by weight and at temperatures up to a maximum of 65 °C. When cleaning by circulation, the velocity shall be restricted to 0.5 m/s, because at higher velocities the efficiency of the inhibitor will be reduced. The ferric ion concentration shall be kept below 0.4% by weight to avoid severe corrosion, and a minimum circulation rate of 0.2 m/s is required to ensure deposits are removed.

Ammonium bifluoride (typically 1% by weight) added to hydrochloric acid is often used to remove SiO₂ (silica). For the removal of scale the acid shall be added in a controlled manner, because the reaction between scale and acid will release gases and heat.

If calcium sulphate and silicate deposits are to be removed an alkaline boil-out may also be required prior to acid cleaning (see Appendix 1).

Restrictions on the use of hydrochloric acid for cleaning are:

- if the ferric ion concentration exceeds 0.4% by weight, some acid should be dumped and fresh acid solution added to restore acid concentration;
- hydrochloric acid shall not be used for cleaning austenitic stainless steel, e.g. AISI 304, 321, 347, 316, 310, to avoid pitting and/or chloride stress corrosion cracking. Parts made of these materials, such as thermowells or valve internals, shall be removed from the cleaning circuit;
- care should be exercised when heating hydrochloric acid solutions because the acid is highly volatile, and the vapour is toxic and corrosive.
- for cleaning aluminium brass bundles, even inhibited hydrochloric acid may cause general attack. The cleaning frequency and the cleaning conditions shall be restricted. The liquid shall not be reused for cleaning steel equipment (see 3.6.1).

3.4.2 Sulphuric acid

Sulphuric acid is less versatile than hydrochloric acid, but is often used when chloride stress corrosion cracking could otherwise occur. It can form insoluble salts, e.g. with calcium. Effective inhibitors shall be used to prevent corrosion of the metallic parts.

Sulphuric acid should be applied in concentrations of 4% to 10% by weight and at temperatures up to a maximum of 75 °C. When cleaning by circulation, the velocity shall be restricted to 0.5 m/s and the ferric ion concentration shall be kept below 0.4% by weight.

Ammonium bifluoride (typically 1% by weight) added to sulphuric acid is used to remove silica.

3.4.3 Citric acid

Citric acid is available in crystals. It is applied for the removal of millscale in new boilers and delicate equipment such as turbine rotors. Although corrosion rates are low, effective inhibitors shall be used.

Citric acid is typically applied in concentrations of 5% to 6% by weight and cleaning temperatures up to 95 °C can be used to reduce cleaning time. Citric acid can also be used to remove copper (see Appendix 1).

Citric acid is suitable for many materials and should be used when austenitic stainless steel parts are present.

For cleaning equipment with internals made of 12% chromium steels (e.g. type AISI 405, 410, 410S) citric acid shall be used only at temperatures below 60 °C.

3.4.4 Sulphamic acid

Sulphamic acid is also a crystalline acid, but its use should be carefully considered due to some known cases of severe pitting corrosion.

3.4.5 Alkaline solutions

Alkaline solutions are used when an alkaline boil-out is applied prior to acid cleaning of boilers (see Appendix 1).

3.4.6 Aromatic solvents

Aromatic solvents may be used for the removal of some tar and polymer products. They should be mixed with an emulsifying agent.

NOTE: Benzene shall not be used as a solvent.

3.4.7 Ethylene diamine tetra-acetic acid

The tetra-sodium salt of ethylene diamine tetra-acetic acid (EDTA) has been used for on-stream cleaning of boilers. Its continuous use is not recommended because unless it is correctly injected and controlled, severe corrosion will occur.

3.4.8 Chelating agents

Chelating agents specifically formulated for the on-stream cleaning of boilers are commercially available.

On-stream cleaning using such chemicals can have the advantage of potentially restoring efficiency without having to shut down the boiler to carry out a conventional chemical clean.

The on-stream cleaning approach has to be very carefully evaluated as the chemicals employed can be very costly and their effectiveness may not always match the suppliers' claims. As with EDTA, their use has to be very carefully controlled.

3.5 INHIBITORS

When acids are used for chemical cleaning, metals will be severely attacked unless a suitable inhibitor is added. The effectiveness of inhibitors is affected by acid velocities, which should normally be restricted to 0.5 m/s. There is also a temperature limit above which the inhibitor will decompose and lose its effect. For this reason inhibited acid solutions shall not be heated with live steam.

Several types of inhibitor are commercially available, such as Rodine and Armohib (for which chemical cleaning contractors may use their own type description). Manufacturers' prescriptions shall be closely followed for the particular application since the inhibitor is only suitable for one type of acid and metal, and some inhibitors give optimum performance only when added to the concentrated acid.

The effectiveness of a proposed inhibitor shall be checked by exposing metal test coupons to the inhibited acid solution (see 3.6).

During the actual cleaning process the continued effectiveness of the selected inhibitor should be checked by immersing a sample of the construction material (e.g. steel wool in the case of carbon steel) in the cleaning solution. After dispersal of air bubbles, the inhibitor is considered effective if no gas bubbles are formed.

3.6 EFFECTS OF CLEANING AGENTS ON CONSTRUCTION MATERIALS

3.6.1 General

Cleaning agents selected for the type of fouling deposit shall also be checked for any unfavourable effect they may have on all the construction materials of the equipment. Acids and alkaline solutions may cause high corrosion rates or other adverse effects; therefore, before starting a cleaning application, a careful laboratory investigation is required in cases where no comparable experience is available.

The testing procedure shall be as follows:

Test coupons of materials similar to the construction materials of the equipment to be cleaned shall be exposed to the cleaning agent for 24 hours. The concentration and temperature of the cleaning agent shall be as intended for the actual cleaning. The inhibitor shall be added to the cleaning agent.

A sample of the fouling deposit shall also be added, since this may influence the attack on the test strips. It also allows the cleaning efficiency to be tested.

In order to obtain the effect of velocity during actual cleaning, the sample should be stirred continuously.

From the weight loss of the test coupons the corrosion rate can be determined, which should be not more than 0.01 mm in 24 hours. Any tendency towards pitting shall also be observed. The inhibitor will need to be replaced and the test repeated until an acceptable rate is found.

Table 3.6 may be used as a guide. Sections 3.3 and 3.4 give further limitations.

Chemical cleaning should not last too long, as some attack will always occur. Different materials may also be affected at differing rates, e.g. with 12-Cr steel internals in a carbon steel column, the inhibitor should be adequate to protect both the carbon steel and the 12-Cr steel.

Table 3.6 Suitability of chemical cleaning agents

	Concentration (% wt)	Maximum temperature °C	Carbon steel and low alloy steels	Cast iron	12-Cr steel	Austenitic stainless steel	Cu/Ni	Aluminium	Monel	Aluminium brass
Inhibited hydrochloric acid	2-5	65	+	+	x **	-	x	-	-	-
Inhibited citric acid	6	95	+	+	x *	+	+	x	+	+
Inhibited sulphuric acid	4-10	75	+	+	+	+	+	-	+	-
Alkaline solutions		70	+	+	+	+	+	-	+	x
Organic solvents			+	+	+	+	+	+	+	-

x = restricted

* = 60 °C maximum, (see 3.3.3)

+

** = Ambient temperature only, (see 5.2.1)

- = unsuitable

3.6.2 Effects on special materials

Chemical cleaning of special materials mentioned in (3.6.2.1 through 3.6.2.5) shall be considered on a case-by-case basis.

3.6.2.1 Tantalum

Tantalum equipment shall not be cleaned with acids or alkaline solutions. Acids may cause embrittlement due to absorption of the released hydrogen, and alkaline solutions will cause serious corrosion.

3.6.2.2 Titanium and silver

Any type of cleaning of titanium and silver or silver-lined equipment which causes disturbance of the initially formed protective film shall be avoided, since serious corrosion may occur.

3.6.2.3 Glass lining

Glass-lined equipment shall not be cleaned with alkaline solutions and its steel jackets shall not be cleaned with acids, for reasons mentioned in 3.6.2.4.

3.6.2.4 Coatings and linings

For certain coatings and linings, acid cleaning of the uncoated side shall not be performed. The hydrogen gas formed may penetrate through the steel wall and cause loosening and/or spalling of the coating or lining, e.g. acid cleaning shall not be used on the shell side of heat exchangers having a baked-on coating on the tube side.

3.6.2.5 Graphite

Graphite equipment shall not be cleaned with oxidising chemicals or with cleaning solutions containing phenolic or cresolic compounds.