CHEMICAL CLEANING OF METALS

Metal equipment must be cleaned from time to time to prevent damage and maintain efficiency of operation. The chemical cleaning of metals has a number of advantages over mechanical cleaning methods. The greatest of these are that the metal equipment to be cleaned doesn't need to be dismantled and reassembled, and the cleaning doesn't damage the equipment, leaving areas that are more vulnerable to corrosion than before.

Metal equipment typically gets both organic and inorganic substances deposited on it, coming from various lubricating oils, corroding metal, deposited product, deposits from hard water etc. These are typically removed in a five step process, although this is varied depending on the exact nature of the scale (deposits).

Step 1 - Cleaning with alkali
Typically this is done with caustic soda (NaOH), and results in the removal of all polar substances such as fats and oils. The vegetable and animal oils are converted to glycerol and soap, and the petrol-derived oils (such as hydraulic oil) are "emulsified" (suspended in water) by any of a variety of emulsifiers.

Step 2 - Rinsing
This loosens the deposits on the metal and washes away both the alkali and the substances that it has removed.

Step 3 - Cleaning with acid
Acids remove any ionic deposits from the metal. The choice of acid depends not only on the price and how strong it is, but on what anion is associated with the hydronium ion. Sometimes a more expensive acid is used because the anion of the cheaper alternative forms an insoluble salt with the ion to be removed. Moreover, some substances, such as silicates, are hard to remove with acid and so a specialised acid (in this case HF) has to be used.

Step 4 - Rinsing
Again, this loosens deposits and removes the cleaning chemical ready for the next stage.

Step 5 - Passifying with alkali
The cleaned metal is now in a highly reactive state, and so it must be coated with a protective layer to prevent corrosion. This is usually done by reacting the metal with an oxidising agent (usually an alkali) to form an oxide layer on the metal. This layer cannot be further oxidised and so protects the metal underneath.

The metal equipment can once again be used as it was designed. The scale that was deposited on it is washed away as dissolved ions which are harmless to the environment.

INTRODUCTION

Chemical cleaning is a process which primarily uses chemical solutions to remove foulings from inside plant and equipment. The circulation of chemical cleaning solutions without dismantling existing process equipment, a process known as CIP (cleaning-in-place), is used daily in New Zealand industry.

Every day perhaps $50 000 of industrial chemicals are consumed in the cleaning of process vessels, particularly in the food processing industries. Caustic soda (NaOH) and nitric acid (HNO$_3$) are used extensively for cleaning stainless steel dairy equipment. Heavy industry provides the more diverse applications of cleaning chemistry, so this article will concentrate in this area. For example, during each of the chemical cleans on Huntly Power Station's four boilers, a semi-rig and trailer load (over 20 000 litres) of concentrated hydrochloric acid is pumped in, and over half a tonne of iron corrosion product is removed. These boiler cleans occur once every two to ten years, depending on operation and feed water quality.

Types of deposits
Foulings can be simple or complex mixtures of organic and inorganic substances. Organic deposits include:

- slime and algae found in cooling water circuits
- animal and mineral fats and oils
- heat denatured product (e.g. proteinaceous burn-on of milk products), sometimes caused by process stream leakage.
- hydrocarbons, polymers and coke formed in various process streams.

While the following are common inorganic deposits:

- carbonates, oxides and hydroxides of Ca, Mg, Fe, Mn, Cu and Zn, e.g. haematite Fe$_2$O$_3$ and geothite FeOOH.
- phosphates of Ca, Mg and Fe, e.g. hydroxyapatite (Ca$_3$(PO$_4$)$_2 \cdot$Ca(OH)$_2$)
- sulphides of Fe, Cu and Zn
- sulphates of Ca and Mg
- silicates (usually complex) e.g. acmite Na$_2$O$\cdot$Fe$_2$O$_3 \cdot$4SiO$_2$
- corrosion products.

The foulings can exist in a range of forms from light, soft, easily removable "sludge" types to hard, complex, layered "scale" types such as magnetite (Fe$_3$O$_4$) coatings in boiler tubes. Temporary rust preventatives and corrosion resistant "Japan Black" pipe fitting coatings (a mixture of carbon black, resins and solvents) become "foulings" in the sense that they must be removed prior to commissioning plant. Often such coatings are designed to be chemically resistant, which poses additional problems.

Why spend money cleaning?
Both the plant and the equipment are cleaned for a number of reasons. These are to do with maintaining the plant so that it can continue to be used in a cost-effective manner. The following sections list the main reasons for which plants are cleaned.

Plant Commissioning
Before a plant can begin operation, any protective coatings, fabrication and installation debris or scales present are often removed. If this was not done either the efficiency of production would be lessened or the plant itself could be damaged. One example is the removal of rust and "Japan Black" coatings from high pressure gas compressor suction pipework.

Plant Utilisation
If fouling is allowed to continue, in some cases catastrophic failure of plant can occur resulting in complete and extended loss of use. This is the main concern with magnetite (Fe_3O_4) foulings in steam generator plants such as those in power station boiliers. As the magnetite scale grows with service time it increases the thermal resistance of the generator tube to the imposed heat flux. Once the magnetite gets thicker than 50 m this can result in the metal temperature of the generator tube exceeding the yield temperature for the given stress conditions. Tube failure (**Figure 1**) results and hundreds of thousands of dollars per day of power generation capacity is lost in downtime.
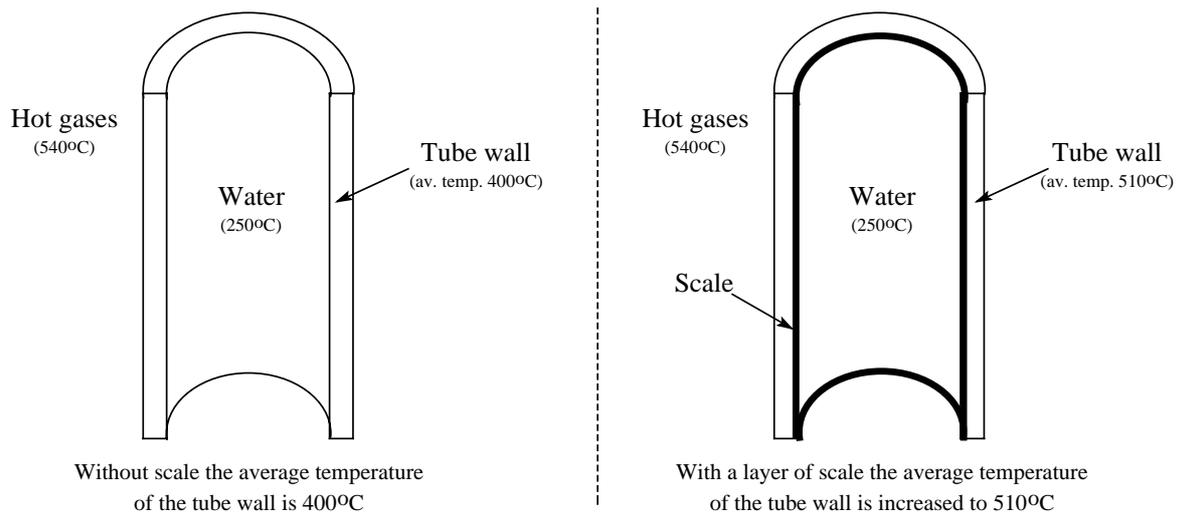

Without scale the average temperature of the tube wall is 400ºC

With a layer of scale the average temperature of the tube wall is increased to 510ºC

Figure 1 - The effect of scale on tube temperature

Plant Efficiency/Energy Conservation
Increasing fouling levels decrease efficiency by changing process conditions from those designed. Some examples are reductions in heat transfer and general corrosion which result in partial or complete loss of equipment output.

Plant Maintenance
Frequently a plant must be cleaned before it can be serviced to ensure that it is safe to work on. Chemical cleaning is selected over manual cleaning (e.g. hydroblasting at 10 000 psi water pressure) depending on the nature and extent of the scale and the physical configuration of the plant. The choice of cleaning method often depends on cost effectiveness.

THE BASIC PROCESS

The metal that is to be cleaned is treated in a five step process. This involves washing in alkali, rinsing, washing in acid, rinsing again and then passifying the metal, i.e. making it less reactive so that it is less susceptible to further corrosion.

Step 1 - Cleaning with alkali
The aim is to remove all organic substances so that a hydrophilic, inorganic surface remains. When degreasing, all hydrophobic (polar) impurities, which include dirt, metal chips, metal

dust, polishing fat, corrosion resisting oil and including process product, must be removed to ensure an effective acid clean.

Although water immiscible solvents such as trichloroethylene ($CHCl=CCl_2$) or trichloroethane ($CH_2Cl\text{-}CHCl_2$) are sometimes used, warm aqueous alkaline solutions are the most cost-effective. The natural fats, i.e. vegetable and animal used in industry consist of esters of glycerol and higher fatty acids. These esters are "saponified" (converted into glycerol and the sodium salt of the relevant fatty acid) by caustic soda (the alkali usually used). These substances are water soluble and hence are removed by rinsing. The mineral fats (oils) are petroleum products and are not decomposed by alkalis but are dispersed and suspended in alkaline solutions. This process is called emulsifying (see **Table 1**).

Table 1 - Some common emulsifying and sequestering additives

Species	Comments
Non-ionic surfactants, e.g. nonyl phenol ethoxylates $CH_3(CH_2)_8$ —⬡— O—CH_2CH_2 $(OCH_2CH_2)_nOH$ (n = 8 - 10)	Used as wetting agents and detergents.
Sodium gluconate $$\begin{array}{ccccccc} H & OH & H & & H & OH & \\ H-C-C-C-C-C-C-O^-Na^+ \\ OH & H & OH & OH & H & O \end{array}$$	A degreasing aid that also acts as a sequestrant (antideposition agent) for iron and water hardness cations in caustic solutions by complex formation.
Sodium phosphates, silicates and carbonates, e.g. sodium hexametaphosphate, $Na_6(P_6O_{18})$ trisodium phosphate, $Na_3PO_4.12H_2O$	These are used less frequently due to their low solubility in caustic concentrate caused by the common ion effect.

Step 2 - Rinsing
Before and after each chemical step, high flow water flushes are required to physically remove loose or softened material before the subsequent stage. It should be noted that the chemicals do not do all the work: cleaning is a physiochemical process.

Step 3 - Cleaning with acid
Now that the surface is hydrophilic, the inorganic scale (usually calcium or iron based) is then softened and/or dissolved by application of an appropriate acid blend. Acids typically used are given in **Table 2**.

Acid selection
Selection of the acid is primarily dependent on scale (deposit) type, although the physical turbulence available, solution temperature, and the metallurgy of the equipment are also of importance. In addition, price is also considered: mineral acids are cheaper and, because of their high ionisation, can be used at room temperature, whereas organic acids, being much

less strongly ionised, are used at temperatures around 90°C to effect their chelating (complex-forming) properties on the scale.
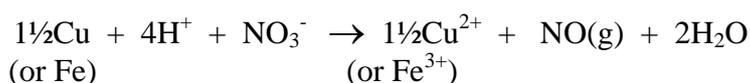
Organic acids are only used when there is a probability of corrosion damage by a mineral acid.

Table 2 - Some acids used in chemical cleaning

Mineral acids	Organic acids
H_2SO_4 sulphuric	HCOOH formic
HNO_3 nitric	CH_2COH ‖ O HO—C—COH ‖ O CH_2COH ‖ O citric
HF hydrofluoric	
NH_2SO_3H sulfamic	
H_3PO_4 phosphoric	HOC—COH ‖ ‖ O O oxalic
NH_4HF_2 ammonium bifluoric	
HCl hydrochloric	$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$ EDTA

For example, monoammoniated citric acid (pH 4) has little tendency, compared with HCl (pH 1), for hydrogen embrittlement of chloride-induced stress corrosion cracking.

HCl acid is the most commonly used acid, and is always used for the cleaning of mild steel. The aggressive chloride (or sometimes fluoride) anion associated with the hydrogen ion is the key to the efficiency of an acid for scale dissolution. However, hydrochloric acid is too aggresive for some applications. Unfortunately, the protective chromium oxide layer on stainless steel is corroded by the halide, and thus stainless steel corrodes as quickly as mild steel. For this reason, HNO_3 (an acid of similar ionisation) is used widely for stainless steel pickling and cleaning. It is an oxidising acid and actually increases the protective Cr_2O_3 layer thickness of stainless steels. However, while this oxidising capability is useful with stainless steels, dilute nitric will rapidly corrode copper bearing alloys and mild steels.

$$1\tfrac{1}{2}Cu \; + \; 4H^+ \; + \; NO_3^- \; \rightarrow \; 1\tfrac{1}{2}Cu^{2+} \; + \; NO(g) \; + \; 2H_2O$$
$$(or \; Fe) \qquad\qquad (or \; Fe^{3+})$$

$$\downarrow \; air$$

$$NO_2 \; (brown \; toxic \; gas)$$

In the case of iron-containing scales including haematite (Fe_2O_3) and magnetite (Fe_3O_4) an acid blend containing a 1 to 10% solution of is used for 4-8 hours at 60°C. Few acids, even

at similar concentration and pH, have affinity for rust removal. "Strong", highly ionised acids such as nitric or sulphuric aren't necessarily any good just because they have a lot of H^+ ions available. The solubility of iron oxides in these acids is not very high. Sulphuric acid relies on the relative solubility of the underlying FeO and Fe metal to physically lift (H_2 evolution helps) the above higher oxide layers off as solid sludge. The process is shown diagramatically in **Figure 2**.
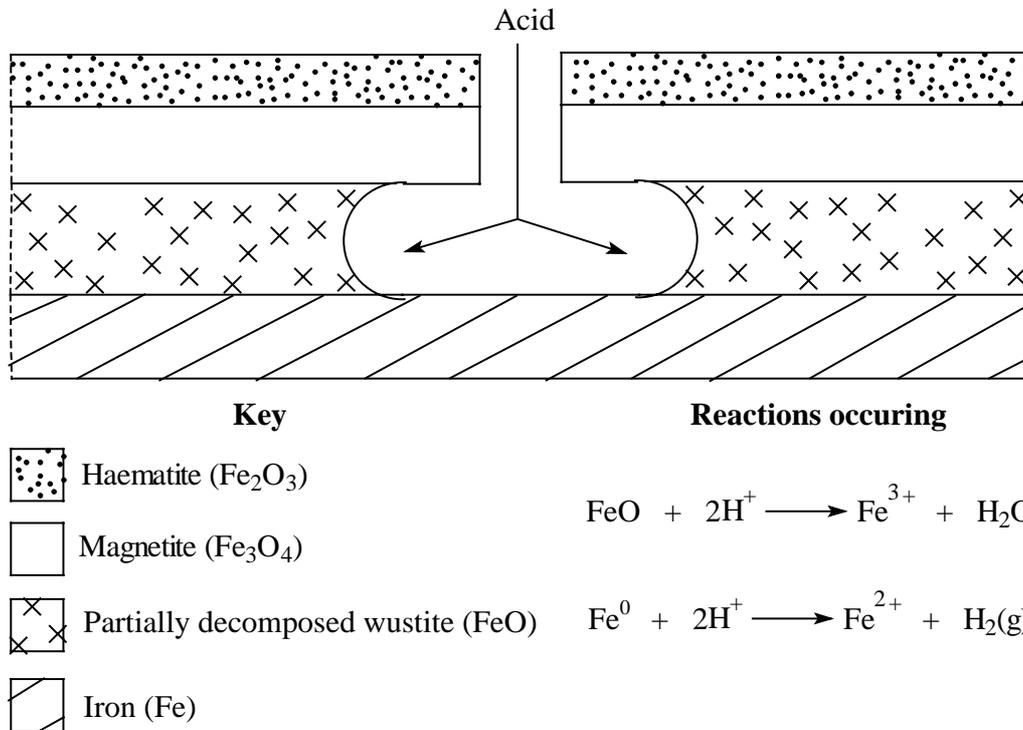
Acid

Key

Haematite (Fe_2O_3)

Magnetite (Fe_3O_4)

Partially decomposed wustite (FeO)

Iron (Fe)

Reactions occuring

$$FeO + 2H^+ \longrightarrow Fe^{3+} + H_2O$$

$$Fe^0 + 2H^+ \longrightarrow Fe^{2+} + H_2(g)$$

Figure 2 - Pickling in acid

Typical Acid Clean on a Boiler Scale (Fe_3O_4)
When an iron boiler which has become coated with iron and copper ions is treated with hydrochloric acid, the following reactions occur. The changing concentrations of the various metallic species are shown graphically in **Figure 3**. This cleaning can involve volumes of 30 000 - 120 000 litres of acid solution and should be done once every five to eight years.

 (a)[1] $Fe_3O_4 + 8HCl \rightarrow FeCl_2 + FeCl_3 + 4H_2O$
 (b) $Fe^{3+} + Cu° \rightarrow Fe^{2+} + Cu^+$
 (c) $Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+}$
 (d) $2Fe^{3+} + Fe° \rightarrow 3Fe^{2+}$ (corrosion)
 (e) $Cu^{2+} + Fe° \rightarrow Fe^{2+} + Cu°$ (corrosion)
 (f) $2H^+ + Fe° \rightarrow Fe^{2+} + H_2(g)$ (corrosion)

In (a) the magnetite is two-thirds Fe^{3+} (ferric) and one-third Fe^{2+} (ferrous). However, as the scale is removed to reveal bare metal, the metal rapidly reduces the ferric ion while further corroding itself (d). Any copper present will be oxidised by the Fe^{3+} acting as an oxidant

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[1] The ^{0} indicates that the metal is in its elemental state.

(b,c). Cupric ions are also unstable with respect to bare steel, and so they replate as metallic copper before the acid solution can be drained (e). This copper must be picked up in a subsequent (alkaline) step.

The classic acid corrosion mechanism (f) can occur when the base metal underneath the scale is uncovered. This reaction is easily minimised (up to a 99% rate reduction) by addition of a corrosion inhibitor blend. These inhibitors (often cationic) tend to adsorb to the electronegative metal surface to form a thin film that inhibits attack.

Ferric and cupric ions from the dissolved scale attack the bared steel surface by pitting corrosion (d,e). This can sometimes result in localised damage and greater weight losses than the inhibited acid corrosion. To overcome this, reducing agents can be added to the cleaning solution to reduce the ferric ions before they attack the base metal. For example the "ene-diol" grouping of ascorbic acid is a very efficient reductant for Fe^{3+} ions in acid cleans.

In summary, the iron is treated with an inhibited acid solution. This results in a conversion of iron and copper ions to Fe^{2+} and Cu^o. The Fe^{2+} is removed in the subsequent washing step and the copper is removed later with alkali. The acid clean is complete when chemical analysis shows that the acid strength has stabilised and the concentration of the dissolved scale species (e.g. Fe^{2+}) has reached a plateau. This indicates that the metal surface is now predominantly clean.
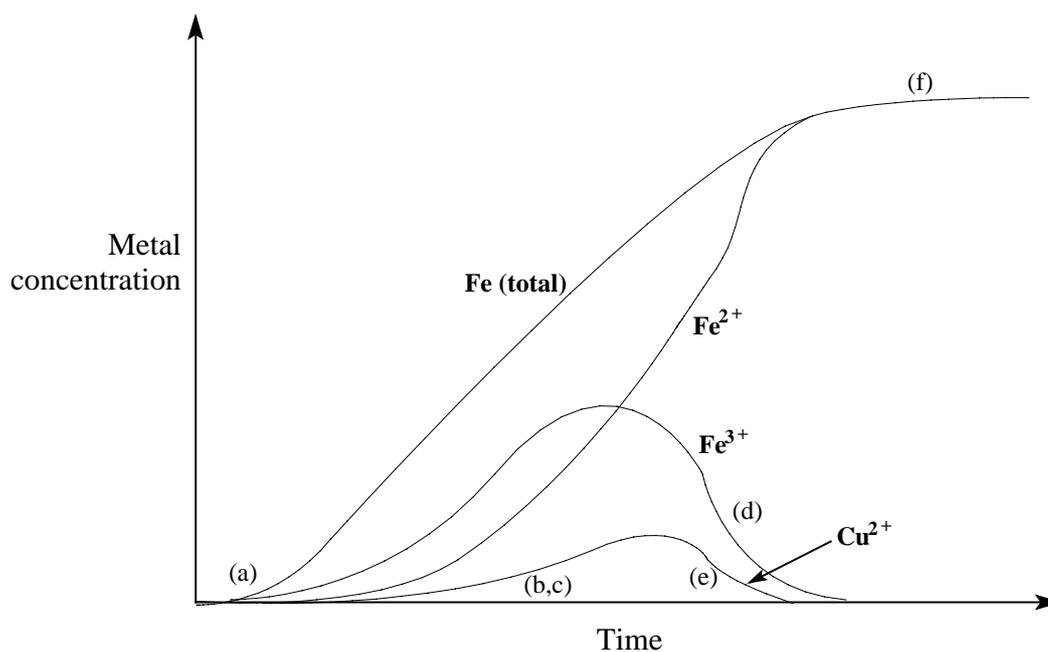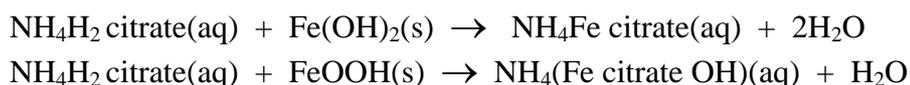

Figure 3 - Changing metal ion concentrations during acid cleaning

Step 4 - Rinsing
After the acid stage, a water rinse is required to remove any loose debris or sludge as well as removing residual chemical. The dilution of the residual chemical solution can often break up the weaker complexes (e.g. $Fe(H_2O)_3(Cl)_3$) to form insoluble hydroxides such as $Fe(OH)_2$, which on air oxidation will produce FeOOH and flash rerusting. To minimise this, the vessel may be drained under an inert atmosphere of nitrogen and a small amount of sequestrant (e.g. monoammonium citrate) could be used to mop up residual iron in the initial rinse.

$$\text{NH}_4\text{H}_2\,\text{citrate(aq)} + \text{Fe(OH)}_2\text{(s)} \rightarrow \text{NH}_4\text{Fe citrate(aq)} + 2\text{H}_2\text{O}$$

$$\text{NH}_4\text{H}_2\,\text{citrate(aq)} + \text{FeOOH(s)} \rightarrow \text{NH}_4(\text{Fe citrate OH})\text{(aq)} + \text{H}_2\text{O}$$

Step 5 - Passivation with alkali

After the acid clean, the ferrous metal is in an active, easily corrodable state. A thin adherent iron oxide layer needs to be reformed as a productive barrier and this is achieved using a hot alkaline solution containing 0.1-1% oxidant. Choices of oxidant are many, but the more common ones are sodium nitrite, hydrogen peroxide, air and sodium bromate.

Care must be exercised when selecting a passivation solution, as some oxidant reaction byproducts can preclude uniformity of the new barrier. For example, halides are known to strongly adsorb to the metal surface so ClO_3^-, BrO_3^-, OCl^- are not good passivators. Persulphates ($\text{S}_2\text{O}_8^{2-}$) are also very powerful oxidants, but they are metallurgically dangerous because they tend to release sulphuric acid on decomposition, which then corrodes the metal.

In the previous boiler clean example given, the replated copper would be removed in the passivation stage by oxidation and complexation in a strongly ammoniated citrate solution, e.g.

$$3\text{Cu}° + \text{excess NH}_3 + \text{BrO}_3^- + 3\text{H}_2\text{O} \rightarrow 3\text{Cu(NH}_3)_4^{2+} + \text{Br}^- + 6\text{OH}^-$$

The cupric ion is stabilised as a tetrammine complex as well as by the citrate.

The steel is also oxidised (dissolved air is useful here) in the alkaline conditions to become passive and this interim passive film prevents gross rerusting until the unit is ready to go back on-stream.

Some special considerations

Scales (deposits) caused by hard water can vary enormously in structure and ease of removal. CaCO_3 in the scale assists the acid process because the CO_2 evolved helps lift the layers above. Calcium and magnesium salts cannot be removed by sulphuric acid as the sulphates of calcium and magnesium are rather insoluble. Siliceous scales near geothermal areas are particularly resistant to acids. Addition of hydrofluoric acid (a fuming, toxic liquid) or ammonium bifluoride (an easily handled solid, NH_4HF_2) can assist here. Hydrofluoric acid is used commercially for etching glass as it dissolves silicates so well.

Sequestering or chelating agents (e.g. gluconate, EDTA, phosphonates) may be used at high temperatures to remove difficult water scales and, in some cases, rust scales. These function by forming complex ions of the metal deposited in the scale, thus making it soluble. As these reactions are equilibrium-controlled, the solvent must be constantly circulating to take away the dissolved complex ions.

ENVIRONMENTAL CONSIDERATIONS

The effluent from chemical cleaning is neutralised by treatment with either sodium hydroxide or sodium carbonate if acidic and with hydrochloric acid if basic. The neutralised solution is then usually treated on site until it meets the effluent disposal specifications of the local authority concerned. Sometimes the customer is unable to process the effluent in this way, so it is processed by commercial waste management professionals. Usually the elements that are of the most concern are phosphorous and nitrogen, as well as the BOD of the effluent.

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