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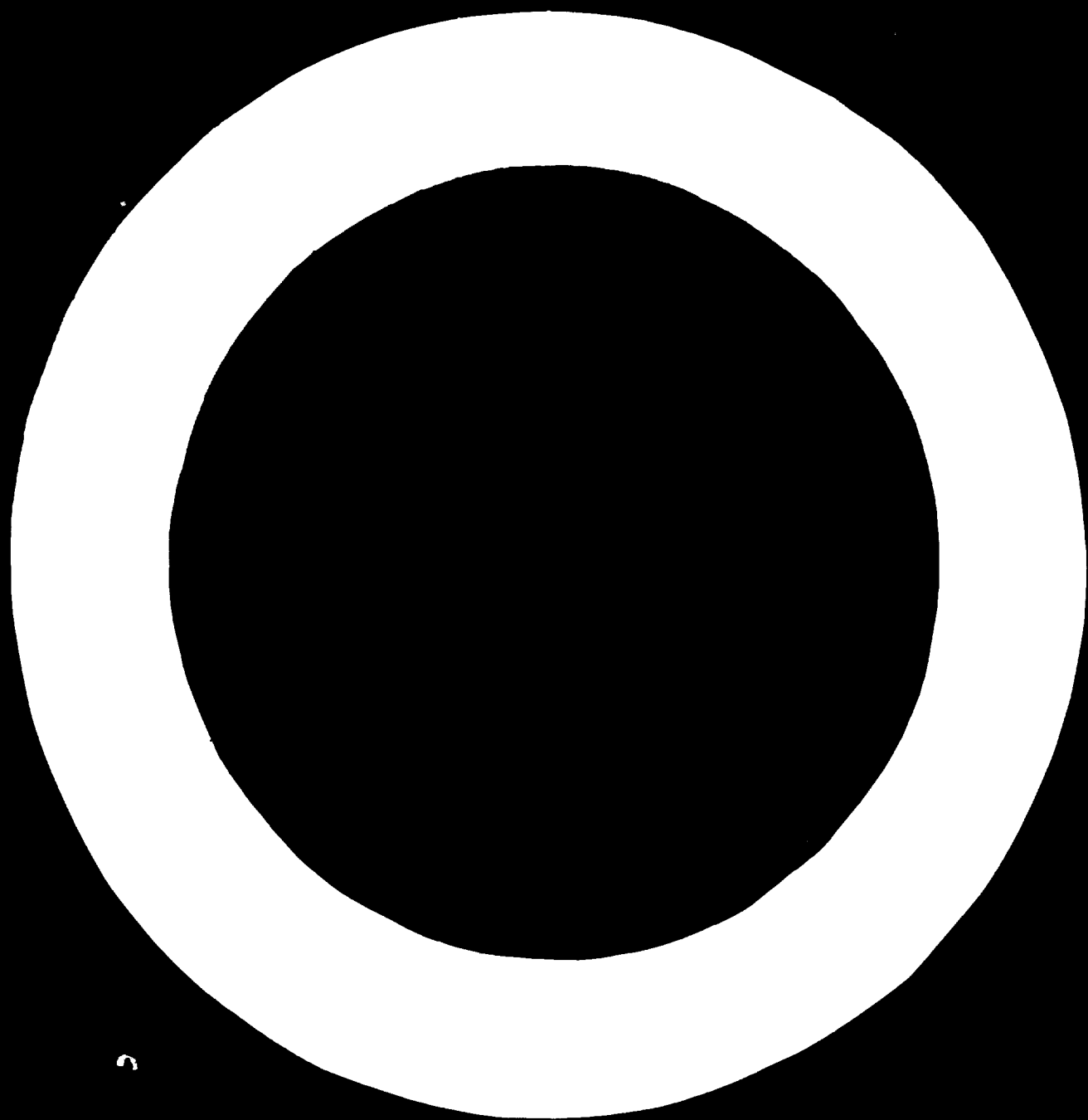
CHEMICAL CLEANING OF PROCESS PLANT

by

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1.0   ## CHEMICAL CLEANING - IT'S ROLE IN REPAIR AND MAINTENANCE OF PROCESS PLANT.

1.1   ### Introduction.

Chemical Cleaning is by no means a new tool in the repair and maintenance of process plant. The Company for which I work has operated successfully in this particular field for almost forty years, and during this period, the use of chemical solutions has become widely accepted as a rapid and efficient way of removing deposits from industrial plant.

At this stage we should define broadly what is meant when we speak of 'process plant' in the context of this paper. This is perhaps best illustrated by reference to the Report of the Process Plant Expert Committee published by Her Majesty's Stationery Office recently. This defines the chief users of the process plant supply industry as follows:-

Chemical Industry

Petrochemical Industry

Gas

Oil

Electricity Generation.

The list is by no means exhaustive, and some of the above sections contain a very wide spectrum of different industries.

The plant itself can obviously consist of a variety of combinations of various items of plant, such as, pipelines, pumps, reactors, contact towers and heat exchangers of all types.

The term chemical cleaning is intended here to include the use of chemical solutions or solvents for the removal of deposits, scales, slimes, or

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other debris, usually from the internal surfaces of process plant.

1.2 Why is Chemical Cleaning Necessary?

If the field of chemical cleaning is considered as a whole, the vast majority of cleaning operations are carried out on heat exchangers, taking the term in it's broadest sense.

Examples of such heat exchange systems are boilers, condensers, coolers, water cooling jackets, heat exchangers, feed water heaters, evaporators, industrial hot water systems, calorifiers and similar plant.

In most types of plant listed above, water is used as the cooling medium, except that, in the case of boilers and heating systems, the water itself is heated. The total effect in all cases is that heat is transferred from an external source into the water. This heat transfer usually takes place through metal surfaces (for example tube walls), which separate the heated and the heating media. When the metal surfaces are clean, heat can easily pass through, but if the metal becomes fouled by scale or deposits, the rate of transfer of heat between the two systems is reduced. In the case of a boiler, the reduction in heat transfer may be sufficient to cause the boiler metal to become overheated, and to fail under the effect of pressure of steam within the plant. In, say, a condenser, however, the results are less serious mechanically, but the unit operates at a much lower efficiency if deposits impair the free transfer of heat

1.2.1. Deposits caused by water.

When water is the heated medium, deposits may result from the effects of heat on dissolved salts in the water, such as hardness salts, which produce scale. Alternatively, in soft water areas, or where water supplies are treated to reduce hardness, the effect of heat may induce

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corrosion of the metal surfaces, and deposits of iron oxide or rust may result. Again, in other areas, local water supplies may encourage organic growths in the plant.

Any of these types of deposit, (and the list is not exhaustive) will reduce heat transfer rates as described previously, and they eventually must be removed in order that the plant may function efficiently and safely.

1.2.2 Product Fouling and other Deposits.

In addition to those deposits formed in heat exchangers which derive from the chemical changes occurring in water used in them, heat exchangers may also become fouled on the product side. For instance, an oil cooler may build up deposits of oxidised or partly decomposed oil on the outside of the tubes through which the cooling water flows. The total effect will, of course, still be that the efficiency of the heat exchanger is reduced. (A later section will deal with means of determining the economics of losses caused by this fouling when compared with the cost of chemical cleaning). Furthermore, fouling can happen in heat exchangers which do not use water in any shape or form. An example of this is in the Furnace type heater often used in refineries. In this case, sulphide deposits usually result from the action of sulphur in the petroleum products forming scales on the parent metal of the heater. These again reduce heat transfer rates, and must be removed in order to restore the heater to it's original efficiency. Reboilers on reformer units are similarly affected. (Special cleaning methods are necessary in order to avoid danger from poisonous gases formed in the cleaning process).

1.2.3. Other Plant Systems which may be Chemically Cleaned.

Besides heat exchangers, many other plant systems may be in need of

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chemical cleaning owing to fouling. For example, long pipelines carrying unstable water supplies often become restricted due to the drop-out of temporary hardness scales. Pipelines similarly may be attacked by corrosion which forms tubercules, restricting the flow of the water in the pipe. Both these types of fouling may be treated by chemical cleaning. Many other systems respond to chemical cleaning, a further example being the removal of deposits from a spray tunnel in which car bodies are cleaned and treated before being finally painted. The circulating spray systems in such a tunnel very often become clogged with deposits, and it is possible to clean the system quickly and conveniently, with the minimum of shut-down period and with no dismantling, by chemical methods. Deposits on the gas side of boilers may be removed by spraying the ash deposits with chemical solution prior to washing down of the unit with treated water.

1.2.4. <u>Precommission Cleaning</u>.

A particular field of chemical cleaning which is sometimes overlooked is that applied to process and industrial plant in general, before the plant is commissioned. While this may, at first sight, have no bearing on the maintenance and repair of process plant, it does, however, play a most important part in preventing teething troubles during the early life of the plant.

New items of process plant are usually supplied in a "commercially clean" state from the manufacturers, but in many instances, the condition deterio-rates during the delivery and erection period.

Furthermore, during the construction of the plant, the interconnecting pipework usually deteriorates, and the whole plant collects general debris
in the shape of dust, weld scale and/general rubbish(including such unlikely

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objects as bottles and old boots).

While chemical cleaning is not the best means of removing the latter foreign matter, it will remove millscale, rust, dust and similar contamination from the plant.

If these contaminants are left behind, it is highly likely that the presence of one or all of them will make itself felt sooner or later during the operation of the plant.

For instance, in boiler plant, millscale (the blue black surface oxide on manufactured steel articles) gradually becomes detached, and can cause not only choking of blowdown valves, but also may promote corrosion processes by the very fact of its incomplete removal. Similarly, the presence of silica in general dust will cause high silica concentrations in the boiler water, which is most undesirable in high pressure plant, and usually results in the wastage of much feed water on initial startup.

Chemical plant, in general, will also benefit from cleaning before commissioning where rust and general debris results in contamination of the early output.

In general, therefore, the need for cleaning both new and used process plant is firmly established, and all that remains is to convince plant managers that the chemical methods of achieving such internal cleanliness is well worth the extra attention necessary.

The following text is written with this one object in view.

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2.0   THE ECONOMICS OF CHEMICAL CLEANING, AND A COMPARISON WITH
MECHANICAL METHODS.

2.1   How much can Chemical Cleaning Save?

It is customary for us to find that as chemical cleaning contractors, we
are frequently called in at the last moment to clean process plant which is
on the verge of becoming unusable due to deposit build-up, or has, in fact,
ceased to operate for the same reason.   It would obviously be much more
expedient if chemical cleaning could be arranged to take place at such a time
that unscheduled shut-downs due to breakdown of the plant are avoided.   It
is, however, difficult to decide the point at which the cost of the chemical
cleaning process, vis-a-vis the monetary saving resulting from such cleaning,
can be balanced.

An article in British Chemical Engineering (1) suggested a practical means
for determining the most economical time to clean heat exchangers.   There is
no reason why this method should not be extended to cover the cleaning of all
process plant where the losses due to fouling can be estimated over successive
fixed periods of time.

The monetary losses due to fouling are plotted against the time axis, where
the units of time are those most convenient depending on the rate of fouling in
the unit.   These monetary losses in process plant operation may result from
either reduced output due to lower efficiency caused by fouling, or by increased
fuel costs made necessary by the extra energy involved to maintain the output.
For example, if the heating coil in an evaporator becomes fouled, the output
from that evaporator will become steadily less as the fouling increases.   The
drop in output results in a direct financial loss which may be recorded as a
monetary loss per day or per week whichever is most convenient.   On the other

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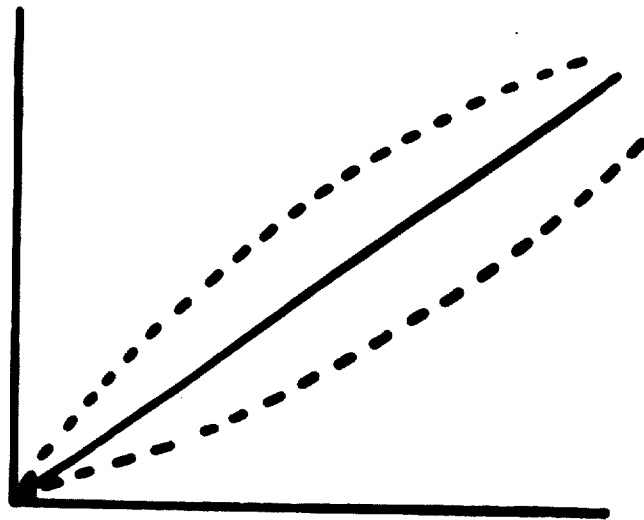
Monetary
loss per
Unit Time
interval.

FIG. 1.

Unit Time.

Area under curve equals
total loss at time 't'.

Monetary
loss per
Unit Time
interval.

FIG. 2.

Time 't'
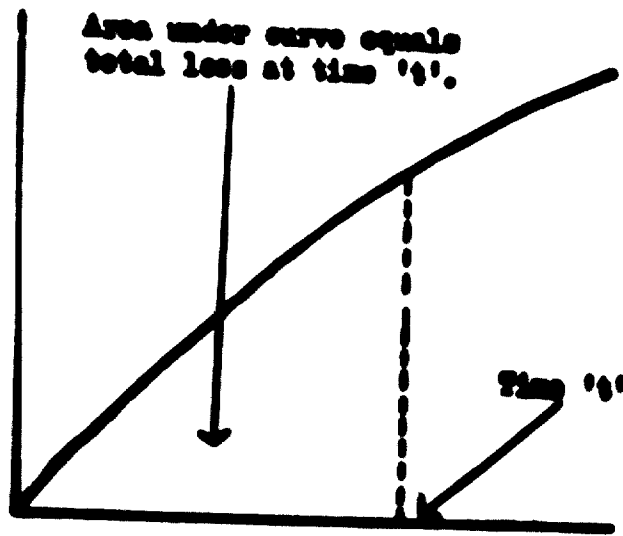
Unit Time.

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hand, it may be necessary to increase the heat input to the evaporator to maintain it's original output, in which case, the monetary loss will be represented by the extra cost of fuel involved to maintain output at the original level.

A curve can therefore be plotted for monetary loss per unit time due to fouling, against those time units. If this curve is commenced immediately following cleaning, the curve will start from the origin and will take one of the three shapes shown in figure one, depending on whether the fouling is increasing at a constant rate, or whether the rate is increasing with time or decreasing with time.

At any period of time, the total monetary loss will be represented by the area under the curve. See figure 2. This area may be calculated by simple graphical means, or may be determined by the use of a planimeter.

If we now consider the curve which is obtained both immediately after cleaning, and which shows a buildup to a maximum when cleaning is again carried out, we should obtain the curve shown in figure 3. It is now obvious that the monetary saving per unit time achieved by the cleaning process can be represented by the shaded area above the curve. (Assuming that the fouling resistance would have remained constant). Thus, at any given instant of time the savings resulting from chemical cleaning can be compared with the monetary losses accumulated to that date.

The most economic time to clean again must obviously be when the total savings resulting from the previous cleaning are equal to the monetary losses incurred by the increase in fouling, i.e., when the two areas above and below the curve are equal.

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Monetary
loss per
Unit Time
interval.

Area under curve is
total saving resulting at
time t_2 from having
plant cleaned at t.

FIG. 3.

Plant cleaned

t_1 t_2

Unit Time

Monetary
saving
resulting
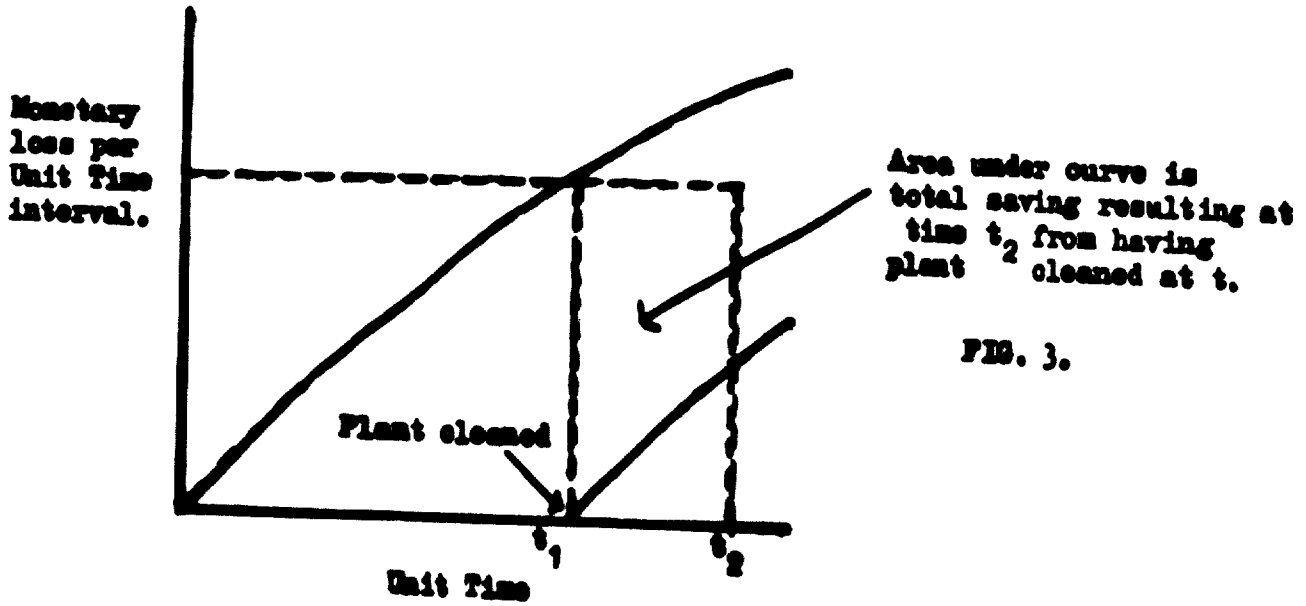from
cleaning.
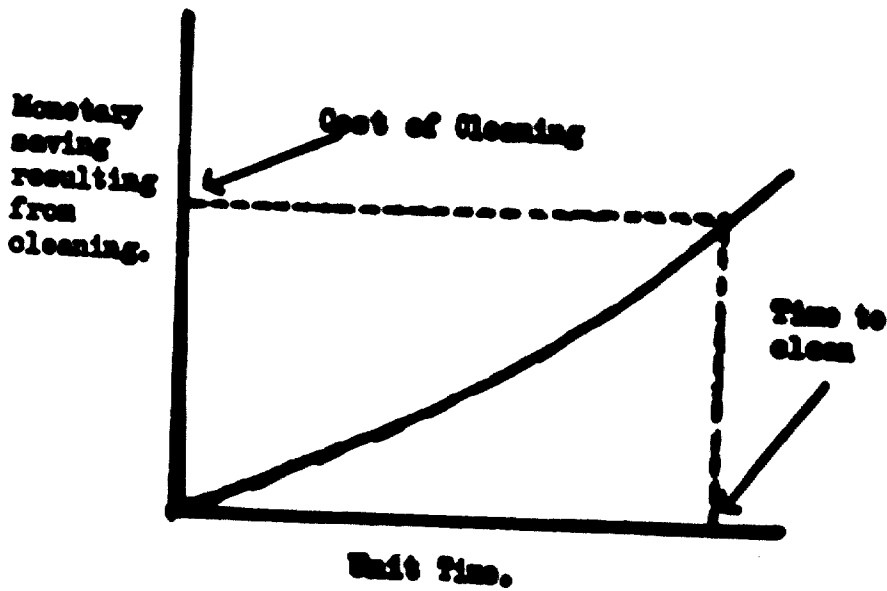
Cost of Cleaning

Time to
clean

FIG. 4.

Unit Time.

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The method must be further developed to include the actual cost of the cleaning operation.   These costs result from the following items:-

Loss of Production ⎫
                   ⎬ due to shut-down for cleaning purposes.
Loss of Efficiency ⎭

Cost of Materials

Cost of Labour

Depreciation on Cleaning Equipment.

For most economical working, the cost of cleaning should be equal to the savings calculated from the area over the curve.   If the cost of cleaning is greater than the saving obtained at any particular time, then obviously the expenditure incurred is excessive, but if, on the other hand, the savings are shown to be greater than the cost of cleaning, then the fouling has been allowed to proceed too far.   In either case, the situation is uneconomic.

A simple method of finding the best time to carry out chemical cleaning is to construct a further curve of the savings against time since cleaning, as in the next diagram.   The values for the savings are derived from the shaded portion above the fouling loss curve shown previously, the area of the curve being calculated as before or by using a planimeter to estimate the saving over specific time intervals.   Time to clean is then obtained from the curve by drawing a line from the value of the cost of cleaning on the ordinate parallel to the absissac.

Where plant needs to be cleaned regularly due to fouling, the above method presents a means of obtaining the maximum aconomic benefit from chemical cleaning. The method assumes that the fouling pattern is the same for each period of operation of the plant even though the rates of fouling may vary according to seasonal changes.   Typical fouling patterns can be produced for each item

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of plant following which the above method is easily applied.

2.2 **The Advantages of Chemical Methods of Cleaning.**

2.2.1. **Mechanical Methods.**

Prior to the wide acceptance of chemical cleaning as a maintenance tool, mechanical methods of cleaning process plant were the only ones available. These included scraping, chipping, rubbing or brushing away debris of all sorts from the plant, the use of "bullets" fired from compressed air for cleaning heat exchanger tubes, while "pigging" was, and still is, widely used as a main means of cleaning long pipelines. Mechanical or physical cleaning has, however, received a tremendous boost by the introduction of high pressure water jetting pumps, in which the cleaning process is accomplished using very high pressure multi-stage pumps to deliver a relatively small flow of water through special nozzles. Amazingly good results have been obtained using this method, limited only by the ability to apply the jets of water to the area to be cleaned. Deposits which sometimes prove unresponsive to chemical cleaning are very often removable by this method.

In certain cases, particularly where very resistant deposits consisting mainly of carbon are concerned, it has been found that a combination of water jetting and the use of chemical solutions is necessary to achieve the maximum efficiency in cleaning. The instances are, however, few and far between, and in general, one method or the other suffices. All in all, most mechanical cleaning involves a good deal of "sweat and strain" while producing mediocre results.

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2.2.2. **Chemical Methods and their Advantages.**

Although most mechanical methods of cleaning are simple to carry out, the results are often far from satisfactory from several points of view. With the introduction of safe chemical methods of carrying out plant cleaning, however, the plant manager has available a most efficient maintenance tool.

The advantages which may be claimed for the chemical methods of plant cleaning when compared with mechanical cleaning may be considered under three main headings:-

      Speed - and hence economy

      Accessibility

      Results

2.2.2.1. **Speed.**

When considering mechanical methods of cleaning plant, the first operation after isolation is always "dismantle", and herein lies the great advantage of the chemical method.

Taking the simplest case, the cleaning of a shell and tube heat exchanger on the tube side, we can compare the two methods as follows:-

	Mechanical	Chemical
Break flow & return connections	2 hours	2 hours
Fit adaptors & circulating equipment	-	1 "
Remove Water Box	6 hours	-
Clean (say 500 tubes)	17 "	2 hours
Flush each tube	3 "	$\frac{1}{4}$ "
Break connections	-	$\frac{1}{2}$ "
Reinstate water box	8 hours	-
Reinstate flow & return	3 "	3 hours
	39 hours	$8\frac{3}{4}$ hours

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With larger plant, the chemical method becomes even more attractive, since both the breaking open of water boxes, and the mechanical cleaning process itself occupy a longer period. The chemical cleaning method, on the other hand, does not require a proportionately longer time to complete the actual cleaning phase - only a greater volume of solution. Furthermore, in the case of heat exchangers, it is possible to chemically clean two units in series - and include the interconnecting pipework in the clean. Similar advantages in time apply in the case of such plant as water tube boilers - the physical action of pushing a brush through each tube in the unit occupying a very much greater time than by the use of chemical solutions. If the deposits are hard - the advantage is even more marked, since the the use of descaling cutters again expands the time required in mechanical operations.

Against this advantage, the chemical clean is more expensive in material costs, and probably in capital costs for equipment. The labour required, while to some extent necessarily of a higher calibre than those used in mechanised methods, are usually less in numbers, so these factors balance. On the credit side, however, the great saving in using chemical means lies in the reduction of outage time, and this can be even further reduced by the fitting of blanked branches on the plant which is required to be cleaned, thereby removing the necessity of breaking flow and return connections each time cleaning is carried out.

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2.2.2.2. Accessibility.

The previous section has compared chemical and mechanical methods of cleaning on plant which can be cleaned by both methods. In more and more instances nowadays, we find that chemical means are the only possible means of cleaning process plant. For instance, many modern water tube boilers have no points of access from which brushing of each tube can be carried out. Compressor cooling water jackets are another example of the advantage of accessibility which chemical methods exhibit. Similarly, when considering a shell and tube heat exchanger, we often find that deposits on the shell side of the tube bundle form a solid mass between the individual tubes. There is a remote possibility of mechanically removing such fouling if the bundle can be withdrawn from the shell, but absolutely none if this is not the case.

This type of fouling often occurs in the modern package type of firetube boiler, and chemical methods are the only way of cleaning this type of plant under these circumstances.

Long lengths of welded pipe run can only be cleaned by physical means if high pressure water jetting equipment and crawler hoses are available, or unless provision has been made for 'pigging'. Simple fill and soak chemical techniques will, in many cases, provide the simple answer to this problem.

2.2.2.3. Results.

The results of the cleaning process, whether it be carried out by mechanical or chemical methods should be judged on the following criteria:-

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(a) Completeness of removal of deposits

(b) Absence of removal of plant materials

(c) Stability of surface after cleaning.

(a) <u>Completeness of removal of deposit</u> is much more likely to be achieved in chemical methods than in mechanical, provided that the correct cleaning solution has been chosen, and that conditions of use have been correct.

Mechanical methods invariably leave small adherent particles of deposit, which eventually on the return to service of the plant act as nucleii for the recommencement of buildup of fouling - hence the "period of immunity" of newly cleaned surfaces is reduced with consequent loss of efficiency, and the earlier need for recleaning.

(b) <u>Absence of removal of the plant materials</u> is obviously essential. While many engineers regard the thought of filling a piece of plant with acid (even though it is inhibited) as completely unthinkable, they will cheerfully allow the valuable components of the same plant to be scratched and scored by scaling tools without any qualms. Using modern inhbitor materials, and when properly applied, chemical methods remove less parent metal from the plant than heavy manual scaling techniques - and leave a surface which is smooth and less liable to corrosion.

(c) <u>The stability of the plant surfaces after cleaning</u> can be ensured by selecting the appropriate passivation method to follow the chemical cleaning process.   These produce a 'deactivated' metal surface which is uniformly covered with a suitable oxide or other stable coating, and so is less susceptible to atmospheric corrosion.

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On the other hand, mechanical methods may leave the metal surfaces in a roughened condition which not only provides nucleii for subsequent fouling, but also has in the crevices and scratches a potential seat for future corrosion.

Conclusion:

Taking all three criteria into account, viz., speed - accessibility - and results, the chemical method has most decided advantages over mechanical means of cleaning, and the most positive of these, speed, becomes more advantageous as plant size increases.

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3.0   THE METHODS USED IN CHEMICAL CLEANING PROCESSES.

3.1   The Materials.

When considering which material to use for a chemical cleaning process, two factors must be borne in mind, namely:-

The material must dissolve or break down the deposit sufficiently for it to be removed from the plant

The material used must not attack the materials of construction of the plant.

3.1.1. Inhibited Acids. The most widely used materials in chemical cleaning processes are undoubtedly the inhibited acids. Obviously, if acid solutions were used alone they would not comply with the second requirement given above, and the metals used in the construction of the plant would be badly affected by the cleaning solution. Inhibited acids are therefore used, and these normally consist of the ordinary commercial acids treated with chemicals which have the effect of allowing the diluted acid solutions to dissolve unwanted deposits and oxides, but prevent the attack by the acid on the metal of construction of the plant. These inhibitors vary very widely, and the earlier ones were often simple inorganic chemicals or even natural products such as glue. Nowadays, however, much more complex materials are used, these are normally organic chemicals which are stable at elevated temperatures and which reduce attack on the parent metal to very small proportions. The most widely used inhibited acid solution is undoubtedly that based on hydrochloric acid. This material was probably the first used in chemical cleaning methods as we now know them, and it still remains the

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most generally acceptable material today.   It is possible to inhibit this acid most effectively using modern materials, and the concentrated acid is easy to handle and is reasonably cheap.

Inhibited hydrochloric acid, when used under the correct conditions, is highly effective for the removal of rust, millscale, and other oxides of iron, water scales and deposits, and it can be used in contact with a wide range of construction materials. Depending on the type of deposit to be removed, and on the time available, it may be used in many cases at ambient temperature.   Solubility of more resistant deposits is however, increased when higher temperatures are used, and the time required for a cleaning operation can similarly be reduced by using hot solutions. It must be borne in mind, however, that the attack on the parent metal also increases with increasing temperature, and it is essential that an efficient inhibitor is used which is capable of withstanding the elevated temperature conditions.   Many commercial inhibitors which are perfectly good at ambient temperatures and indeed up to temperature as high as 140°F. (60°C.) decompose above this temperature.   The result is not only that the parent metal is attacked to a greater extent, but also that the decomposition products of the inhibitors often produce treacly deposits inside the plant.   Selection of the correct inhibitor is therefore essential.

Inhibited hydrochloric acid may be used in admixture with other materials in order to improve its performance when in contact with the more acid sensitive materials.   It may, in certain cases, be used to clean brass, by the addition of suitable chemicals to control desincification.   Similarly, by the addition of fluorides, the effect of the

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inhibited acid solutions on deposits containing silicates is much enhanced. Normally this type of deposit is resistant towards chemical cleaning, and very often presents a difficult problem when considering removal. For this purpose, hydrofluoric acid or one of the soluble fluorides such as ammonium bifluoride or sodium fluoride may be used in proportions of approximately 1% by weight.

Although hydrochloric acid is suitable for use in plant containing carbon steels, it is generally considered to be not suitable where stainless steels are encountered. This is due principally to the danger of stress corrosion cracking which is initiated in austenitic stainless steels by the presence of the chloride ion.. While it is possible that by very thorough washing such danger could be avoided, it is normally considered good practice to avoid the possibility of any such attack.

Sulphuric Acid has also been used extensively in chemical cleaning processes. This acid when inhibited has proved to be a good solvent for many types of deposit, with the exception of the hardness scales, i.e., those containing calcium salts. It is cheaper than hydrochloric acid when considered on a degree of acidity basis, but it is not so easily handled as the aforementioned product. Furthermore, the efficiency of inhibition is not so great as that in the case of the inhibited hydrochloric acids. There is a tendency for the inhibitors available for this material to break down after being in use for a certain period of time. This need not be too serious if adequate chemical control can be ensured for the chemical cleaning process, but this is usually the exception rather than the rule in most operations. Sulphuric acid is, however, often acceptable when dealing with austenitic stainless steel plant, although this too is

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excluded by the Electricity Generating Boards in the U.K.

The use of <u>sulphamic acid</u> overcomes many of the problems inherent in the use of sulphuric acid, in that the acid is a solid material, which is relatively easy to inhibit efficiently, although the solutions are of similar acidic strength to the commonly used mineral acids. It does, however, have the disadvantage that on an acid for acid basis, its cost is relatively high. It may, however, be used for dissolving calcium based scales, since it forms soluble sulphamates unlike sulphuric acid which forms insoluble sulphates. It is, unfortunately, not particularly effective in the removal of rust and millscale, but it is claimed that this action may be increased by admixture with other acids. This, however, complicates the process unnecessarily. It's one great advantage is that despite it's relative strength, it is more easy to inhibit when dealing with the acid sensitive metals. It thus provides an effective reagent for the descaling of non-ferrous metal equipment, and is even permissable where soldered or brazed joints are present.

The other common inorganic mineral acid, <u>nitric acid,</u> is not used to any large extent in every day chemical cleaning, principally because of the difficulty of inhibiting this material. It is, however, used very largely in the precommission cleaning of stainless steel items of plant. In this respect, it is used in admixture with sulphuric and hydrofluoric acids as a paste for removing weld oxides from fabricated structures, again in admixture with hydrofluoric acid as a cleaning agent for the surface of mild steel plant, and it is used alone for passivating such stainless steel fabrication following the chemical cleaning phases.

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Organic acids, and in particular, citric acid, have been widely used in recent years in the chemical cleaning field.   Citric acid is expensive, but it has been used to a great extent in the cleaning of Power Station plant.   It is usually used in 3% solution at high temperature with the pH. value of the solution adjusted to approximately 3.5 with ammonia or ammonium bifluoride.   Under these conditions citric acid is a/most effective solvent for rust and millscale, and, since it has no bad effects on austenitic stainless steel, it is most valuable in cleaning plant containing these materials.   Citric acid for a while enjoyed almost universal acceptance in the post-commission cleaning of power plant, since it was feared that the use of stronger mineral acids was causing damage to the parent metal structure.   It was, however, found that the cleaning effect of this material was not so marked as that of inhibited hydrochloric acid, and the latter material has now returned to favour.   This has been assisted by the discovery that the aggressive nature of well inhibited hydrochloric acid solutions is no greater than that of the inhibited citric acid.

Other organic acids have been used in addition to citric acid. Mixtures of hydroxy acetic acid and formic acid have been used extensively in the United States, and to a lesser extent formic acid and acetic acid have been used by themselves for the chemical cleaning of more acid sensitive materials.

Sequestering agents such as ethylene diamine tetra acetic acid, commonly called E.D.T.A. have been proposed and to a small extent used for some years for the removal of calcium based scales in sugar evaporators and similar plant.   Recently, methods have been developed to use derivatives

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of this material for the removal of iron oxide and copper oxide deposits from boilers. The advantages claimed for such methods are that the alkaline solution is used to remove such deposits resulting in less metal attack and a more passive finish. Unfortunately, it seems necessary to apply such solutions at elevated pressures and temperatures in order to produce results equivalent to the more widely used acid, and under such conditions, the attack rates become comparable with those of the inhibited hydrochloric and similar acids.

3.1.2. <u>Degreasing Agents</u>. In many cases deposits of a greasy or oily nature are required to be removed. Chemical cleaning in such cases is usually accomplished using degreasing solutions which may fall into one of the following three classes:-

> The alkali/synthetic detergent mixtures
> Organic solvents
> Emulsifying solvents.

In many cases where acid cleaning is to be carried out, it is essential to remove grease which is also present in the deposit. This is to prevent the grease or oil from repelling the acid solutions, and hence masking the deposits from the action of the acid.

<u>Alkali/synthetic detergent</u> degreasing solvents are widely available commercially, and make use of such materials as caustic soda, the alkali metal phosphates, the alkali metal silicates, sodium carbonate etc. These materials are used either singly or in admixture together with suitable commercial synthetic detergents. The materials are usually applied as hot solutions to the plant to be cleaned, and agitation or circulation is essential to improve emulsification or solution of the greasy material.

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When choosing a degreasing material, it is still important to take into consideration the material of construction of the plant. Aluminium and zinc and their alloys with other metals will be attacked by solution of too great an alkalinity, and special precautions must be taken in these cases.

The organic solvents used in chemical cleaning processes are usually of the chlorinated hydrocarbon type. These materials are non-inflammable, and have a high capacity for mineral oils and greases. They may be used either by washing the plant with a quantity of the solvent itself, or may be applied as vapours using an external vapouriser to supply vapour of the solvent to be applied to the plant to be cleaned. Inside the plant the vapour condenses, and the condensing solvent washes down the walls of the plant, freeing them from oily deposits. Examples of such solvents are trichlorethylene, perchlorethylene, methylene chloride etc.

The emulsifying solvents are a class of chemicals used in chemical cleaning methods which are most versatile and easy to use. Many types are available commercially, but they usually consist of a kerosene or an aromatic solvent depending on the type of deposit to be removed. The solvent itself contains an emulsifying agent. Oily deposits are removed by application of the emulsifying solvent to the plant, and this results in solution of the oily material in the solvent. As much of the solvent as possible may then be drained off, the remaining solvent being washed away by water. The presence of the emulsifying agent causes the solvent and it's dissolved oil content to be readily emulsified and so removed easily from the plant. It is possible to use premixed emulsions of these solutions to remove oily deposits, such methods usually employing heated solutions.

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<u>Other specialised solvents</u> are used for particular examples of chemical cleaning.   For instance, algaecides may be used for the removal of slime or mould growths in cooling systems.   However, such applications are of limited applicability, and so are generally outside the scope of this paper.

To repeat, therefore, the choice of a material for use in a chemical cleaning process must be examined on the basis of two requirements:-

1.   the material must dissolve or disintegrate the deposits so that they may be easily removed.

2.   the material used must not attack the metal from which the plant is constructed, or must be inhibited to prevent such attack.

3.2   <u>The Methods</u>.

3.2.1.   <u>"Sit & Soak Methods"</u>.   The commonest method, and by far the most widely used method of chemical cleaning processes, is probably the "sit and soak" method.   This is simply to fill the plant which is to be cleaned with a premixed solution of the chemical cleaning reagent. Alternatively, the unit may be filled with water, and the chemical solution or reagent is then added and stirred into the general bulk of the water.   This method can produce good results provided that its limitations are realised.   It obviously works best where there is an evolution of gas resulting from the action of the cleaning agent on the deposit.   This is, of course, the case where temporary hardness scales are being removed, these consisting of calcium carbonate which evolves carbon dioxide when treated with inhibited acids.   The evolution of

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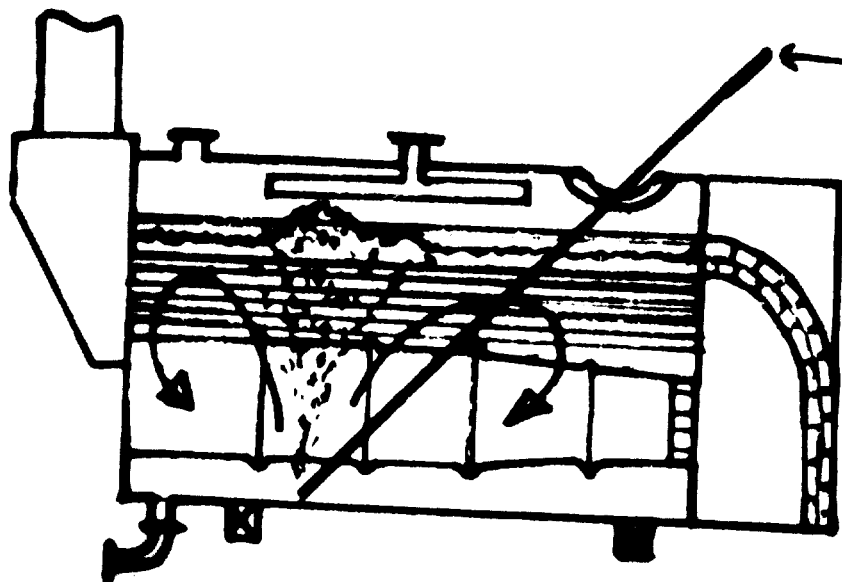
Intermittent injection of air, or nitrogen if available.

FIG. 5.

SECTION 3.2.1.

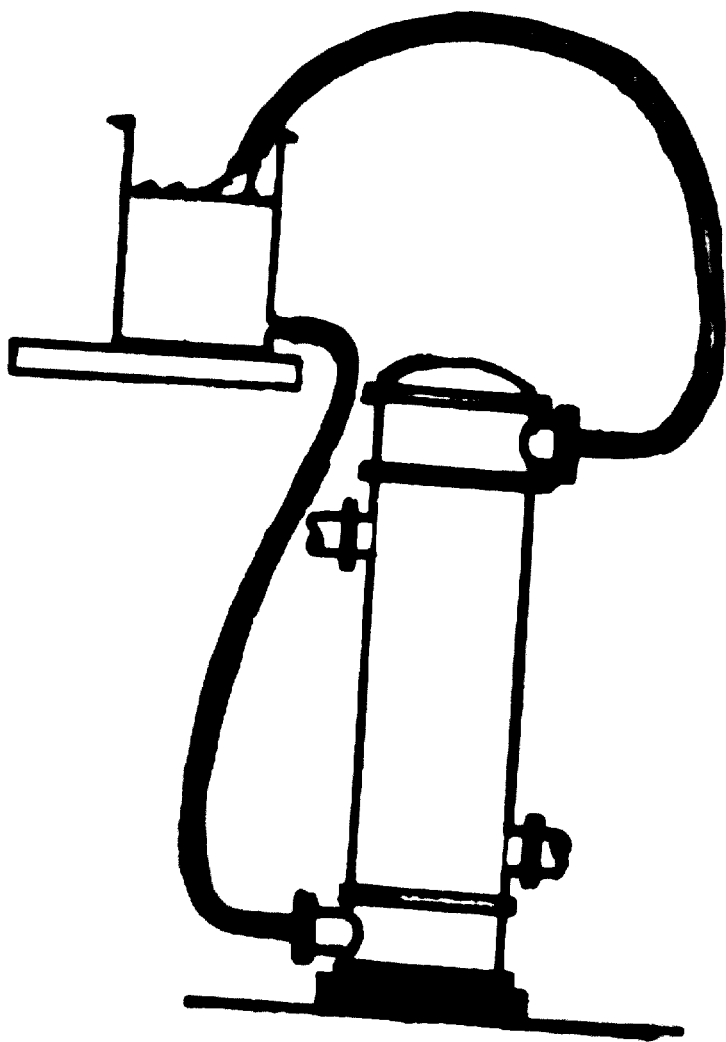'SIT AND SOAK'
CLEANING METHOD
- ECONOMIC BOILER.

FIG. 6.
SECTION 3.2.2.

'AUTOCIRCULATION'
CLEANING METHOD FOR HEAT
EXCHANGER.

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gas generally mixes the solutions rapidly, and prevents local stagnation. The process is allowed to continue until the maximum amount of scale has been dissolved, fresh reagents being added if necessary. The solution may of course be stirred mechanically, or by blowing air through it from a compressor through a suitable discharge tube. See figure 5.

3.2.2. Auto Circulation. This method was developed from the sit and soak method where gases are evolved. Very briefly, it depends on the fact that the density of a column of liquid containing gas bubbles is less than that of the liquid itself. In practice, the equipment to be cleaned is connected from its lowest point to a suitable container in which the chemical cleaning solutions can be placed by means of flexible hoses. The container is placed at a sufficiently high point to enable solvent to flow by gravity into the plant. A return hose is taken back from the top of the plant to the container. In the plant gas is generated because of the reaction between the solvent and the carbonate scales, and the resulting liquid gas mixture flows back to the container by virtue of its lower gravity. See figure 6.

3.2.3. Pump Circulation. Where auto circulation cannot be used, circulation may be induced in the unit by using a suitable pump. See figure 7. In its simplest form a pumped circuit takes off its supply from the lower part of the unit to be cleaned, and returns the cleaning solution to the top of the unit. In this way, stagnation of the cleaning solution is avoided, and a fresh supply of solvent is continuously put into contact with all parts of the plant. It is rarely possible to improve cleaning processes using this method by the velocity effect alone. If sufficiently high velocities are used to scour away resistant deposits, then metal attack would almost certainly take place due to breakdown of the inhibitor film. It is

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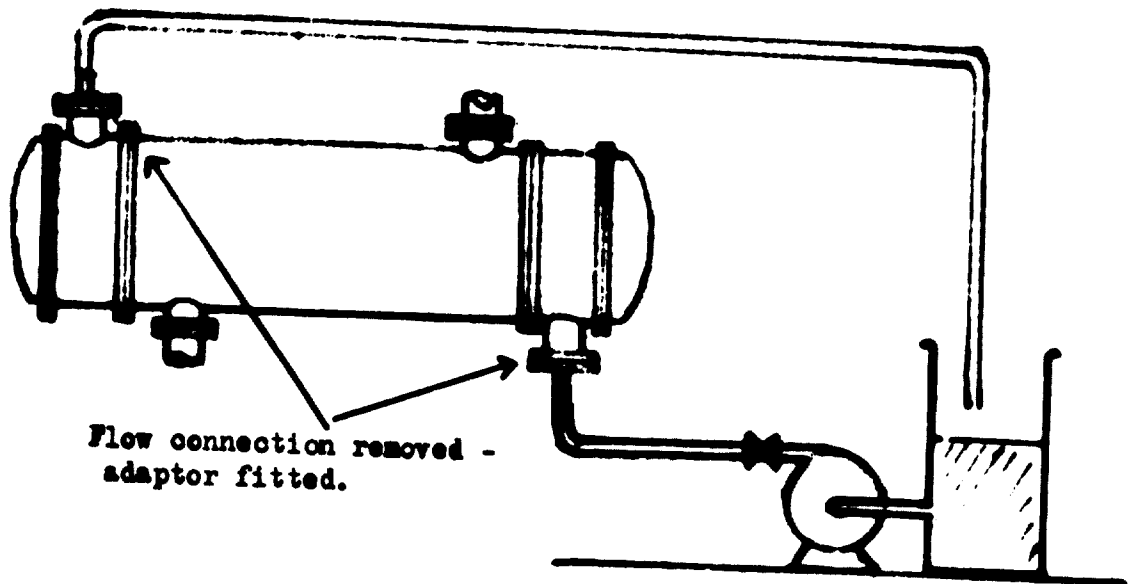Flow connection removed - adaptor fitted.

FIG. 7. SECTION 3.2.3.

PUMP CIRCULATION METHOD - HEAT EXCHANGER.

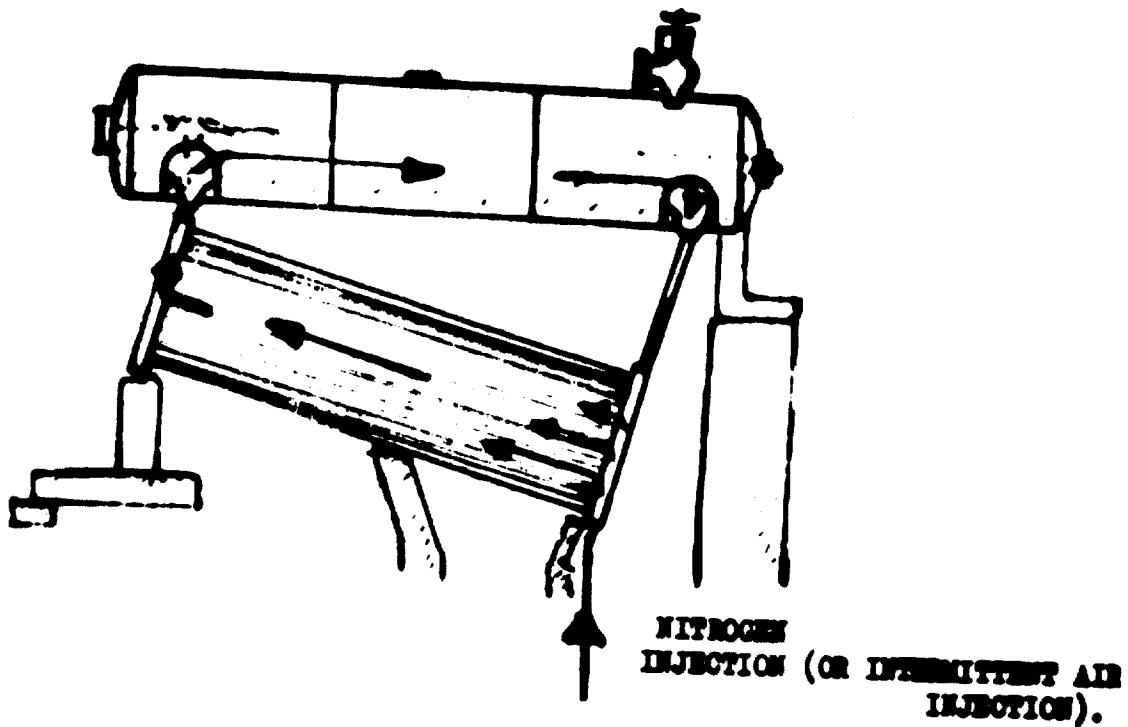NITROGEN INJECTION (OR INTERMITTENT AIR INJECTION).

FIG. 8. SECTION 3.2.4.

GAS INDUCED CIRCULATION - SIMPLE WATER TUBE BOILER.

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important when considering pumped circulation to study the design of the circuit with some care. The factors which must be taken into account when considering this type of circulation are the limiting flow velocity which will be dealt with in a later section, combined with the necessity for recycling the solution within the unit in a reasonable space of time, in order to avoid local stagnation and saturation of the cleaning solution.

3.2.4. **Gas Induced Circulation.** In the section on circulation by auto circulation above, mention was made of using compressed air or similar gases in order to stir up the solution in a vessel or other item of plant. By introducing the air or gas at a suitable place within the plant, it is possible to induce a circulation comparable with that which may be produced when using an external pump. An example of this type of circulation is included in figure 8, which shows the use of air to induce circulation in the chemical cleaning solutions used in a simple water tube boiler design.

3.2.5. **Foam Cleaning Methods.** Several types of apparatus, some of them covered by patents have been designed to produce chemical cleaning solutions in the form of a relatively stable foam. These foams are pumped much in the same way that a liquid may be pumped into the plant to be cleaned. Inside the plant the foam bubbles break on contact with the surface, and the chemical cleaning solution from which the foam was formed, runs back down the walls of the plant as a solution. The advantage claimed for this type of cleaning is two-fold:-

1. The amount of chemical reagent needed is relatively small

2. The weight of cleaning solution inside the plant is small compared with that if the plant were to be filled.

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The first reason may be somewhat of a disadvantage if the types of deposits to be removed are of a nature which will react with the cleaning solvent. The small volume of solution used in this respect becomes a disadvantage, because the solution rapidly becomes exhausted by reaction with the deposit. On the other hand, if the deposit is loosened by the foam, then this may be a valid way of removing it. Similarly, oily deposits may be removed by using a foam made from degreasing solvents. The second advantage is obviously of great value when plant is to be cleaned where the design is such that it will not support the weight of chemical cleaning solution which would be necessary to fill it.

Foam methods, although apparently having advantages, are little used in the United Kingdom.

3.26. **Spray Methods.** In certain types of plants, it may be possible to introduce chemical cleaning solutions in the form of sprays. For example, when it is required to clean a large tank, it is usually possible to arrange for some sort of manifold which will supply solution to all parts of the internal surfaces when charged by a pump. Alternatively, rotating heads may be used which distribute the solutions over the whole interior surface of the vessel. Such methods have the advantage of using only moderate amounts of cleaning solutions, and are thus much more economical than filling the vessel. The same disadvantage may apply in this case, namely, that the solution may become exhausted, and it is necessary to maintain control over this aspect of the operation. Spray methods are obviously limited to the cleaning of surfaces which are easily accessible, for example, the interior of tanks, or the exterior surfaces of surface condensers.

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3.2.7.Paste. Where local areas of plant are to be cleaned, and where it is either impossible or uneconomic to fill the plant, the application of chemical cleaning solutions in paste or gel form may be considered. This method obviously has an advantage over the spray method previously reported in that the application of the material may be confined to small localised areas.   The method employs the usual solutions used for chemical cleaning, namely, inhibited acids, and these are transformed to a paste-like consistency by mixing them with an inert absorbent material such as barium sulphate.   The resulting paste is then applied to the metal surfaces by means of trowels or spreaders, and is left in position for sufficient time for the chemical cleaning reagent to have the desired effect.   It is, of course, obvious that such a method will produce rapid saturation of the chemical cleaning reagent, since fresh supplies of the solution are not repeatedly brought into contact with the surfaces.   The paste is then washed away with water and if the required results have not been obtained, the process is repeated.   Inhibited acids may also be transformed into gels by using suitable organic thickening agents, although the majority of these have only a limited life in such solutions. These gels are again applied by painting or pasting the area to be cleaned. The type of application where these methods are used is, for example, the cleaning of weld areas in fabricated steel tanks, particularly in stainless steel structures. In these cases, the welds are initially ground to remove excess metal but the weld area is usually surrounded by a discoloured surface due to heat staining by formation of oxides.   In these cases, a paste containing sulphuric, nitric and hydrofluoric acids is applied, the pasting agent usually being barium sulphate in this case.   There is, of course, no reason why other chemical cleaning solutions should not be used for paste

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methods, with the one limitation that the amount of fresh solution in contact with the surface to be cleaned is minimal.

3.2.8. Vapour Methods. Mention has been made previously of the use of organic solvents such as chlorinated hydrocarbons for the removal of greasy and oily deposits from industrial plant. If oily deposits are to be removed using liquid organic solvents, then a succession of washes must be employed, since otherwise the residual film of solvent left in the plant will redeposit oil on final evaporation. The use of solvent vapours, however, avoids this disadvantage, since by distilling a solvent, fresh solvent forms continuously on the metal surfaces by condensation. On running down the walls of the vessel, the condensed vapour dissolves the oily material and returns this to the vapouriser. Subsequently, the solvent distills off again, leaving behind the contamination.

The method is valuable where contamination is relatively light, and where the proportion of solvent insoluble materials in the deposit is small. Should there be a high proportion of insoluble material, the usual effect is for vapour treatments to remove the oily matter from the contamination, but leaving behind much of the solvent insoluble material in the form of dusty deposits on the oil-free surfaces. The use of solvent vapours is obviously to be preferred from the economic standpoint, since the amount of solvent employed is very small compared with that needed to carry out repeated washings using the liquid solvent.

In certain types of plant, it may be possible to introduce some of the required solvent into the bottom of the unit, and then to heat this by introduction of a steam coil or similar heater. The solvent vapour then distils and diffuses through the plant, condensing on the cooled surfaces with the cleaning effect

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described previously.   At the end of the process, all of the contamination
within the plant is concentrated in the residual solvent at the bottom of the
unit, and may be drained away, so removing the maximum possible contamination
while using the minimum amount of solvent.

A second type of vapour phase cleaning involves the use of steam as a carrying
agent.   For example, should the plant to be cleaned be in the form of a long
pipeline, steam is blown through the line and cleaning chemicals are injected into
the steam.   Under carefully controlled conditions, inhibited acids may be used in
this method to remove millscale and rust from steel surfaces.   The conditions are
however, quite critical and it is possible, under certain circumstances, to
produce much heavier quantities of metallic oxides than were previously present.
Another aspect of this type of cleaning is, of course, the use of alkali
detergent mixtures in saturated steam for the removal of greasy deposits.   This
process is widely used in cleaning motor vehicles where small portable steam
generators of the coil type are used.   The detergent chemicals are either
introduced into the water supply of such equipment, or may preferably be injected
into the discharge lance of the equipment by use of an ejector device.   The
second method is, of course, preferable since the possibility of choking of the
steam coil by accumulated chemicals is avoided.

3.3   The Equipment.

The equipment required for carrying out chemica cleaning processes may be
divided broadly into the following main headings:-

    Storage

    Transfer

    Mixing and Dissolving

    Circulation

    Disposal

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The factors to be taken into account when the choice of equipment is made are as follows:-

The equipment must be adequate to do the work in the engineering sense.

The equipment must be sufficiently resistant to the materials used to ensure satisfactory performance.

The equipment must not be so heavy or expensive as to make the operation uneconomic.

3.3.1. **Storage.** Normally, in small chemical cleaning operations, the storage of the chemicals to be used presents no problem. The materials are handled and used from the containers in which they are supplied. If somewhat larger operations are to be considered, then some suitable storage tank must be provided in order to achieve maximum economy in the purchase of chemicals. For example, it is much cheaper to buy hydrochloric acid in bulk delivery than by the purchase of smaller containers, and if chemical cleaning operations are being carried out sufficiently frequently to consider the purchase of a storage tank, then obvious economies can result.

The conventional storage tank for aggressive materials such as the concentrated inhibited mineral acids are metal tanks suitably lined with protective material. Usually such lining takes the form of a hardened rubber, and although such tanks are initially expensive, the life is usually long, provided that they are not damaged mechanically. Where it is required that the tank should be portable, however, a tank fabricated from plastic materials is to be desired because of its lighter weight and hence ease of transport. The tank is usually made from fibreglass, lined with a material such as P.V.C., or the tank may be constructed

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from polythene, in which case, no lining is required, although some
mechanical stiffening is usually necessary. The tank is transported
empty to wherever it is required, and is then set up on a firm flat base
and the required chemical is delivered to it by bulk tanker delivery.
A different form of transportable storage tank is provided by the rubber
inflatable type of tank, this takes the form of a pillow-like bag. This
may be transported from site to site, rolled up on a lorry, then once
again, on reaching site, a firm base is provided and the chemical solutions
delivered to the bag from a bulk tanker.

The disadvantage of both types of portable tank is that they are
mechanically not strong, and must be protected from accidental damage.
In the case of the rigid plastic tanks particularly, suitable venting
must be ensured, otherwise collapse of the tank will result on withdrawing
the solution.

3.3.2. Transfer. It is obviously desirable to avoid manual transfer of corrosive
solutions where possible. In small scale cleaning operations, the use of
the containers in which the cleaning materials are supplied is expedient,
but here again, the handling of the materials can be made much less
hazardous by the use of suitable transfer pumps. The simplest way of
accomplishing this transfer when small quantities of material are to be
moved is to use a carboy siphon. The limitation here, of course, is that
the solution containers must be placed at a higher level than the vessel
into which they are to be discharged. Alternatively, a small carboy
emptying pump of the dip type may be used. This consists of a small pump
mounted on a tube which is long enough to reach to the bottom of the
container to be emptied. The small pump is electrically or air driven

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and can usually deliver the contents of the carboy or vessel to a height of approximately ten feet above the container. Where larger supplies are to be transferred, the use of a chemically resistant positive displacement pump is advisable. The materials are obviously quite corrosive in their concentrated state, so that complete resistance to the chemical solution is essential in this case. Another suitable pump for transporting relatively small quantities of acids is, for example, the Duplex Pump, a positive action diaphragm type. The pump will deliver approximately ten gallons per minute of solution against a head of 100 lbs. sq. in. Where larger quantities of solution are to be transported, a centrifugal pump is of course, desirable, here again, the construction materials must be resistant to the concentrated chemicals. When using pumps for the transfer of the chemicals, the usual practice is to use chemically resistant hoses for the purpose of transporting the liquid. Natural rubber hoses are available, which are suitable for most of the reagents used, and these may be secured by mechanical clips of the Jubilee Clip type. Obviously this method is not practicable where high heads are encountered and in this case suitably lined metal pipework must be employed.

3.3.3. Mixing & Dissolving. Before the chemical reagents may be used in the chemical cleaning process, they must either be suitably diluted with water, or if they are solid, they must be dissolved in the solution. It is, therefore, common practice to use a mixing or dissolving tank in the chemical cleaning circuit. These obviously will not necessarily be of very large capacity compared with the circuit to be cleaned, since the solution used to fill the cleaning circuits may be introduced either

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batch-wise, or continuously, using suitable techniques.   For ease of
portability, the most popular tanks in use for this purpose are usually
made from fibreglass with suitable resin lamination.   Such tanks are relat-
ively rigid and easily transported.   They are also sufficiently resistant
to the chemicals in use to be satisfactory for the purpose.   They are, of
 course, not as strong mechanically as lined metal tanks, but the ease of
transportation far outweighs this disadvantage.   A mixing tank is usually
provided with a suitable branch outlet so that it may be connected to the
circulating pump used for the circulation of the chemical cleaning circuit.
The same type of tank may be used for dissolving solid chemicals prior to
their addition to the plant.   Usually this is achieved by introducing
(preferably) hot water into the tank and mechanically agitating the
solutions with either compressed air or suitable paddles.   Where larger
quantities of materials are to be handled, the use of a suitable mechanical
stirrer is preferable.   Alternatively, good mixing may be achieved by use
of pump to agitate the contents of the tank, the pump withdrawing solution
from the base of the tank and discharging it back into the top.
The most convenient size of tanks for this type of operation is usually
found to be between 100 and 300 gallons (500 - 1,500 litres).

3.3.4. Circulation. The choice of circulation equipment is, of course, governed
principally by the size of the circuit.   The quality of equipment to be/
used will depend principally on the economics of the cleaning process. For
example, if the single operation is being considered, it is obviously not
practical to consider the purchase of an expensive chemically resistant
pump.   In such circumstances, it is quite adequate to employ a simple

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centrifugal pump and to accept the fact that the pump efficiency will fall off rapidly in use owing to erosion on the surfaces. On the other hand, if repeated cleans are to be considered, it would be wise to look into the purchase of a totally resistant pumping unit, many of which are currently available on the market.

In addition to the chemical requirements of the pumping unit, the normal hydraulic factors must be taken into account. It will be shown in a later section that certain limits of circulation velocity are required, and these must be borne in mind when choosing the equipment. Secondly, the head at which the circulating pump will operate must be taken into account, and a pump which is capable of achieving this head must be chosen. Where large quantities of solution are to be circulated, it is desirable to consider the use of multiple small pumps rather than of one large unit. In this way, the success of a chemical cleaning operation is not jeopardised by the failure of the one unit, sufficient circulation being available using the remaining units to ensure satisfactory completion. In choosing pumps for such multiple operations, however, the usual hydraulic conditions must be taken into account, e.g., a pump with a flat efficiency curve should be chosen.

The motive power for the pump is, of course, chosen to suit local conditions, but a diesel engine is often used for chemical cleaning operations, since they are most flexible and are usable in most situations.

3.3.5. Disposal. Disposal of the used chemical solutions usually presents one of the most difficult problems associated with the use of the process. It is possible by neutralising the used solutions chemically to discharge them

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into the normal drainage system. Alternatively, it is usual to store the used solution in tanks similar to those used for storage of the undiluted chemicals until they can be removed by tanker for disposal elsewhere. Consultation with the appropriate authorities in good time avoids trouble later.

3.3.6. <u>Truck Mounted Pump Complex</u>. It is common in the United States to use complexes built up of the various items and these are mounted together on a suitable truck unit. Pumping equipment, chemical mixing tanks and storage, heating equipment and the necessary valves and manifolds are all interconnected permanently in such an arrangement.

This arrangement is most convenient when repeated cleaning operations of a similar type are envisaged, but is rather inflexible in character should operations of a different type and size be contemplated.

3.3.7. <u>Heating Equipment</u>. It is often desirable to use warm solutions to accelerate the rate of dissolution of deposits in chemical cleaning processes. For small operations, a suitable steam generator may be used, these produce steam or hot water by direct flame heating in a small coil type boiler. They may be used to heat tanks containing chemicals by either direct injection or by producing hot water in place of steam. Alternatively, direct flame type heaters may be used, which use bottled gas supplies to heat tanks of water by the use of suitable plate type heaters. This type of equipment is less susceptible to breakdown than the steam generators, but are usually somewhat slower in raising temperature.

Electrical methods of heating may, of course, be considered where

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adequate power supplies are available, immersion type heaters being most widely used.

Where large operations are envisaged, the use of such portable types of heating methods are not suitable and the use of a small portable steam boiler is required. These can often be mounted on a suitable trailer unit and are thus available for towing to the site where they are required.

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4.0   ## THE CRITERIA FOR SUCCESSFUL CHEMICAL CLEANING.

The criteria on which the success of a chemical cleaning operation is judged are:-

The complete removal of the deposit or contamination.

The absence of attack on the parent metal of the plant.

The production of a stable surface following the cleaning process.

4.1. Removal of the Deposit. It is obviously most advantageous if a solvent can be found which will completely dissolve the contamination. This is, unfortunately, infrequent. In areas where water of high temporary hardness is present, deposits usually consist of calcium carbonate scales, and in th case alone, almost 100% solution of the deposits can be achieved using inhibited hydrochloric acid. Usually, however, the deposits encountered are only partially soluble, and the best that can be expected in these cases is, that sufficient of the deposit will be dissolved to ensure the breakdown of the remainder. Under these conditions, the insoluble residue is usually left in the form of a sludge where it can be washed away by adequate flushing.

It is good practice to test the deposit prior to choosing the chemical cleaning solvent, if suitable samples of the contamination can be obtained. It must be remembered, however, that the conditions pertaining in a beaker in the laboratory are very much different from those which will be encountered in the plant itself. For instance, if pieces of scale are broken away from a boiler, and are then tested in the beaker in a laborator it must be remembered that, in the latter circumstance, all sides of the deposit are attacked by the cleaning solution. In practice, however, only

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the outermost face is exposed at any one time to the action of solvent. This, of course, means that in the laboratory a more favourable indication is sometimes found than is achieved in practice. In general, it can usually be taken that if 50% solbility is achieved under laboratory conditions, then the process has a reasonable chance of success in practice.

Solubility can, of course, be increased by using heated solutions, and this is very often employed in practice as a means of dissolving the less soluble deposits with inhibited acids. It is, of course, essential in these cases to consider the second criterion, namely the absence of attack on the parent metal when choosing suitable solvents. Many chemical cleaning solvents which are perfectly satisfactory at ambient temperatures, are totally unusable at elevated temperatures.

If the deposit contains a large proportion of insoluble residues, then flushing must be adequate to remove this at the completion of the process. This is especially necessary if pendant superheater or similar type tubes are being cleaned. In these tubes, the acid cleaning solution will deposit insoluble residues at the bends, which may cause subsequent blockage of the tubes. It is therefore most essential that the flushing rates following chemical cleaning are sufficiently high to remove these insoluble residues. In the small bore tubes, it is usually accepted that a flushing rate of 4 ft. per second is desirable to achieve satisfactory removal of debris. It must be emphasised, however, that this is usually too high a circulation rate for inhibited acids and the safe maximum value in most cases for acid circulation is accepted as 1 - 2 ft. per

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second in small bore tubes.

In many cases where the deposit is not 100% soluble, increased solubility may be achieved by a suitable pre-treatment.   This is the case, for instance, where sulphate scales are involved.   These are not very soluble in the inhibited acids, and it is common practice to 'boil out' the unit containing such a scale with an alkali treatment prior to the application of inhibited acids.   The application of alkali modifies the scale and often improves the solubility of the subsequent acid process.

It is also beneficial to boil out items of plant which have been chemically cleaned where the deposits are not 100% soluble.   This is very often a much more positive method of removing adherent remaining deposits where all surfaces cannot be contacted by jets of water subsequent to the acid cleaning process.   In these cases, it is normal to employ alkaline solutions - say, of up to 1% caustic soda solution, or 3% or 4% sodium carbonate solution, these solutions being boiled out at atmospheric pressure in the plant to remove adherent residues.   This treatment is again followed by copious rinsing with water.

4.2. Prevention of Attack on Parent Metal.   The second criterion is, of course, that the chemical cleaning solution shall not damage the item of plant to be cleaned.   In cases of doubt, it is advisable to consult chemical cleaning consultants who will advise on the type of cleaning agent best suited for the purpose.   However, there are general rules which assist the choice of an inhibited acid for removing a particular type of deposit when in contact with different metals.   A table detailing the more common chemical cleaning reagents, and the metals in contact with which they are

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suitable, (bearing in mind the deposits which are required to be removed) is appended.

In general, the inhibitors now available for use with mineral acids are extremely effective, provided that they are used in accordance with the directions given. It must, however, be borne in mind that some inhibitors are only effective at lower temperatures, and may break down if the temperature is raised. In addition to the destruction of the inhibiting properties of the material, such breakdown is often accompanied by the formation of 'treacly' deposits which add to the difficulties within the plant

4.2.1. **Flow Rates.** When considering the use of inhibited mineral acids, the effect of velocity mentioned above must be carefully considered. As the velocity of the cleaning solution is increased, the extent of corrosion by direct attack of the cleaning reagent on the parent metal is increased linearly, Under most circumstances, it is usually accepted that the safe maximum value for the circulation of chemical cleaning solutions in relatively small pipework is 1 ft. - 2 ft. per second (0.3 - 0.6 metres/second). It must be borne in mind, however, that this figure cannot be applied to pipework of all sizes since, obviously, the turbulence effect produced in small pipework by such velocities is very much greater than those produced in large bore pipework. In such cases, consideration of the Reynolds Number is a much more effective criterion, but such consideration is beyond the scope of this present paper. Where the safe velocity of circulation has to be

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exceeded because of other factors within the plant (for instance, at the inlet points of plant where reasonable overall circulation is required) more severe attack can be expected, but there are special processes available on the market which reduce such attack to extremely low levels by the use of sophisticated techniques. Such a process is the VECOM KF Process patented in England and on the Continent. Details of the process are available on request. It must be borne in mind that the factors affecting both the removal of the deposit, and the extent of attack on the parent metal are the same. These are, velocity, time, temperature and concentration. It is essential that the values chosen for these factors are carefully considered in order to achieve the best overall results.

4.3. Preparation of a Stable Surface Following Cleaning.

4.3.1. The need for 'Passivation!' When the metallic surfaces of a plant have been chemically cleaned, those surfaces are usually in a very active state, and unless some positive action is taken, the surfaces will rapidly deteriorate, and much of the benefit of cleaning will be lost.

This is particularly so in the case of plant made from mild steel, when freshly cleaned surfaces are very susceptible to rerusting. This comment applies to both inhibited acid cleaning processes, and solvent degreasing (alkaline degreasing agents leave steel surfaces in a reasonably passive condition for reasons which will become obvious later). Where solvent degreasing has been carried out, the steel surfaces are completely freed from oily residues, which would, in

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ordinary circumstances protect the metal from deterioration by rusting (which is, of course, caused by moist air).

Acid cleaning processes on the other hand, completely remove all oxides from the surfaces of the parent metal, in addition to those deposits which are the reason for carrying out the cleaning process. These surface oxides are the barrier between the parent metal and the oxygen in the air. Under reasonably dry conditions, the oxides prevent continued attack on the metal - and hence are essential to the preservation of the plant. At the completion of the cleaning process, we have a metal surface which has been stripped not only of its undesirable deposits, but also of its surface layer of protective oxides.

In many instances, a protective oxide layer will commence to grow immediately upon returning the plant to service, but generally speaking, it is better to follow the chemical cleaning process with a "passivation" phase which is designed to produce a stable, uniform oxide layer on all of the exposed metal surfaces.

In the case of boiler plant, this is most important, since a boiler relies for its survival on the uniform layer of magnetic iron oxide formed on those surfaces in contact with water. Rupture of this uniform layer leaves a small area of the metal surface which is most susceptible to attack - hence on-load corrosion. Fortunately, in boiler plant, it is relatively easy to produce a uniform film by "boiling out" the unit, but in other plant, this method is not so readily available.

4.3.2. **The passivation methods available.**

Mild Steel. Two basic methods of passivation of mild steel

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are available for use after acid cleaning.   The first method aims
to promote the growth of a uniform oxide film, the second to convert the
surface film to a stable compound, the most widely used being the
phosphate process.

Stable oxide formation takes place on mild steel particularly well in
the presence of alkalies when heat is applied, and the film is even more
uniform if reducing conditions can be achieved.

For example, in the case of boiler plant, both of these conditions can
be achieved, and it is usual to 'boil-out' the unit following an acid
clean.   For this purpose, the water in the plant is treated with
alkaline chemicals.   In the case of low pressure plant, a 1% w/w
solution of sodium carbonate may be used.   If it is possible to apply
up to 100 ppm of sodium sulphite and maintain this, then the desirable
reducing conditions are also achieved..

The boiler is then heated, and pressure is raised without exporting
steam.   All drains are operated from time to time.   The process is
continued for 12-24 hours, at the end of which time, the unit is blown
down under pressure, and ventilated to dry quickly.   A stable dark
grey or black surface is obtained.   Higher pressure units usually
boil out with trisodium phosphate, and start with lower concentrations,
about 1,000 - 2,000 ppm, again using sulphite or hydrazine as reducing
agent.

Where the unit cannot be heated under pressure, some degree of
passivation is obtained by simply heating alkaline solutions in the
unit under atmospheric pressure.   For instance, a 1% sodium carbonate

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solution may again be used.   If direct heating of the plant is not possible, then circulation of a hot solution of alkali is advisable. Temperature should be maintained in the circuit as high as possible by injection of steam if available.

Where the heat is not available, the methods available become rather more complex.   Essentially they depend on the sequestration of iron from the metal surface, and oxidation under alkaline conditions.

If no other method is available, circulation of a cold 3% solution of sodium carbonate will reduce the tendency towards rerusting, and will effectively neutralise any remaining acid residues.

Conversion coatings, the most widely used of which is the phosphate conversion, are produced by the action of chemicals on the clean metal surfaces.   A very presentable phosphate film may be produced on mild steel by immersing it in, or filling units made from it, with a warm dilute solution of phosphoric acid (2% w/w) for about 15 minutes.

A bright silver grey surface results, which is quite stable when dry. (more stable phosphate coatings may be obtained by using proprietary mixtures which incorporate metal phosphates, giving much more permanent results).   Here again, the phosphate coatings produced by the simple method are very good - provided that heat is available.

Phosphate coatings may be produced in the cold, but they are much less stable and are not uniform.

Other Metals.   The passivation of metals other than mild steel is not of quite such importance since, in general, the rate of deterioration of the cleaned surfaces is not so rapid.

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Stainless steel should, however, be passivated following cleaning, **and this is** usually accomplished by immersing it in nitric acid of about **20% v/v** strength. Brass and other copper alloys sometimes need **treatment** following cleaning, and this is usually accomplished by **applying** oxidising agents such as sodium dichromate in sulphuric **acid solution.**

4.3.3. The Importance of Flushing. **Where** acid cleaning processes (and in fact all chemical processes using aqueous solutions) have been **carried** out, it is most essential to remove all traces of cleaning chemical **from the** plant before attempting passivation.   The flushing process should **also** remove all debris resulting from the loosening of deposits in **the** plant, otherwise this debris will mask the underlying surfaces and **prevent** the passivation from acting on these.

Where mild steel has been cleaned, particularly when hydrochloric **acid** has been used, the metal surface is very active, as explained before. **Furthermore,** on draining away the acid solution, the metal surface **is** **left** covered with a film of acid containing dissolved iron. If this **is** washed away by filling the unit with water, the iron in the film **will be** thrown out of solution in the form of a gel on the metal surface. This gel will trap chloride residues from the cleaning solution, **and these** will not be flushed away by subsequent washes.   The chloride **residues** remain on the metal surface and are very active in promoting **subsequent** rerusting.

This can be avoided by including a complexing agent for iron, for

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example, citric acid in the first rinse water applied to the unit.
This solution at 0.1% concentration will prevent this drop-out of
iron gel.

Subsequent plain water washes remove all traces of iron and chloride
residues.   The passivation process then has the most positive chance
of producing a stable uniform protective surface.

All in all, the treatment of the plant subsequent to the cleaning
process is almost as important as the clean itself - the proverbial
'ha'porth of tar'.

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5.0.   EXAMPLES OF CHEMICAL CLEANING PROCESSES.

5.1.   Descaling of a Heat Exchanger.

The type of descaling solution required should be decided taking into account the analysis of the deposit which is causing the fouling, together with the materials of construction of the plant.   Table 1 will give general guidance.

If possible, some estimation of the amount of chemical required should also be made, since this will indicate how much cleaning solvent will be needed to dissolve all of the deposit.   Whenever possible, it is best to carry out tests to determine the solubility of the scale, and also to estimate the amount of chemical required so that the solution does not become exhausted

A very rough estimate of the amount of inhibited hydrochloric acid required in the case of a typical steam plant deposit may be obtained by assuming that the unit weight of the concentrated acid will remove unit weight of the scale.

5.1.1. Using Pumped Circulation.   The circuit is set up as shown in Figure 7 Section 3.2.3.

(i). Isolate the unit by closing the water inlet and outlet valves, or by spading off the lines.

(ii). Drain the Unit.

(iii). Connect the delivery of the pump by hose or pipework to the lowest available point on the water inlet side.   If no suitable connection is available, it may be necessary to break the line and fit an adaptor.

(iv). Connect a return pipe or hose to the highest available tapping

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point, e.g., thermometer pocket socket on the water outlet pipe. Return this pipe or hose to a small tank, which should be fitted with a suitable branch at the bottom to enable it to be connected to the pump suotion.

(v). Connect pump suction to the tank.

(vi). Fill the tank with the descaling solution diluted with water to the recommended level as shown in the appended table. Mix well.

(vii). Pump the solution into the unit.

(viii). Continue repeating items (vi) and (vii) until the unit is full and liquid returns to the tank by the upper or return hose.

(iv). It is possible, with some experience, to fill the unit by adding water and chemical solution continuously in the required proportions to the tank, while the pump is running.

(x). Circulate the diluted solution by pumping. If further addition of chemical is required, this may be added to the tank from time to time.

(xi). The completion of the process will be indicated in the case of a carbonate scale by the cessation of gas evolution.   Check that this is not due to complete neutralisation of the acid solution by adding some of the cleaning solution from the tank to a piece of washing soda, (sodium carbonate) in a suitable jar.   If no gas is evolved, further addition of acid is required..

(xii) In the case of non-carbonate scales, the washing soda test will also confirm that the acid is still active. However, no easily recognised sign indicates the end of the process in this case, and only experience will indicate the amount of contact required if no chemical analysis is possible.

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(xiii). If the solution can be tested for residual acidity, the completion of the process is indicated when the acidity does not decrease further with time. In cases where rust deposits are being removed, the iron content of the solution may be determined, and the stabilisation of this figure again indicates completion of the process. (Examples of typical chemical monitoring of cleaning processes are shown later).

(xiv). Drain the unit, neutralising the effluent if necessary with caustic soda liquor, soda ash or lime <u>after the solution has been drained fro</u> <u>the unit.</u> Do not add neutralising agents to the solution in the uni

(xv). Flush out the unit thoroughly with clean water, preferably from the top downwards in order to remove all undissolved debris.

(xvi). Fill and drain the unit with clean water, repeating until all acid residues have been removed.

(xvii). In order to completely remove all traces of acid, the final fill may be made with a solution of a suitable alkali such as soda ash at a level of 1 lb. per 20 gallons of water.

(xviii). Thoroughly wash out any instrument connections or "dead legs" in the unit before putting it back on line.

5.1.2. <u>Using "Auto Circulation" Methods - without pump.</u> The circuit is set up as shown in Figure 6. Section 3.2.2. In this method, circulation relies upon the evolution of gas resulting from the action of the cleaning agent on the scale - which only happens with carbonate, or temporary hardness deposits. The method is applicable only to this type of deposit.

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(i)   Isolate the unit as in 5.1.1. (i).

(ii) Drain the unit.

(iii) Site the cleaning solution tank so that it's outlet branch is higher than the top of the unit to be cleaned.

(iv) Connect the outlet branch of the tank to the lowest suitable point on the water inlet side, using hose.

(v)   Fit a hose to the highest available point on the water outlet, and return this to the top of the tank.

(vi) Fill the tank with a suitable diluted solution of the inhbited acid continuing until a return of solution is obtained from the return hose.

(vii) The return of solution via the top hose will continue until gas evolution ceases, since the specific gravity of the acid/gas mixture is less than that of the liquid alone.

(viii) When gas evolution stops, add further inhibited acid to the tank, if the action recommences, continue making additions of fresh solution until the process is completed.

(ix) Drain the unit, and flush out thoroughly as described in sections 5.1.1. (xv - xviii) previously.

5.2   Descaling of an Electrode Steam Boiler by the 'fill and soak' Method.

This type of boiler provides steam by heating water by passing an electric current through it between two electrodes.
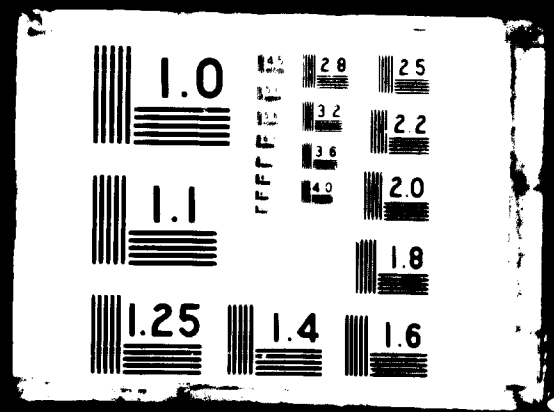
The materials of construction make it necessary to use a cleaning solution which is less aggressive than inhibited hydrochloric acid, and inhibited formic acid is acceptable.

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Safety Valve
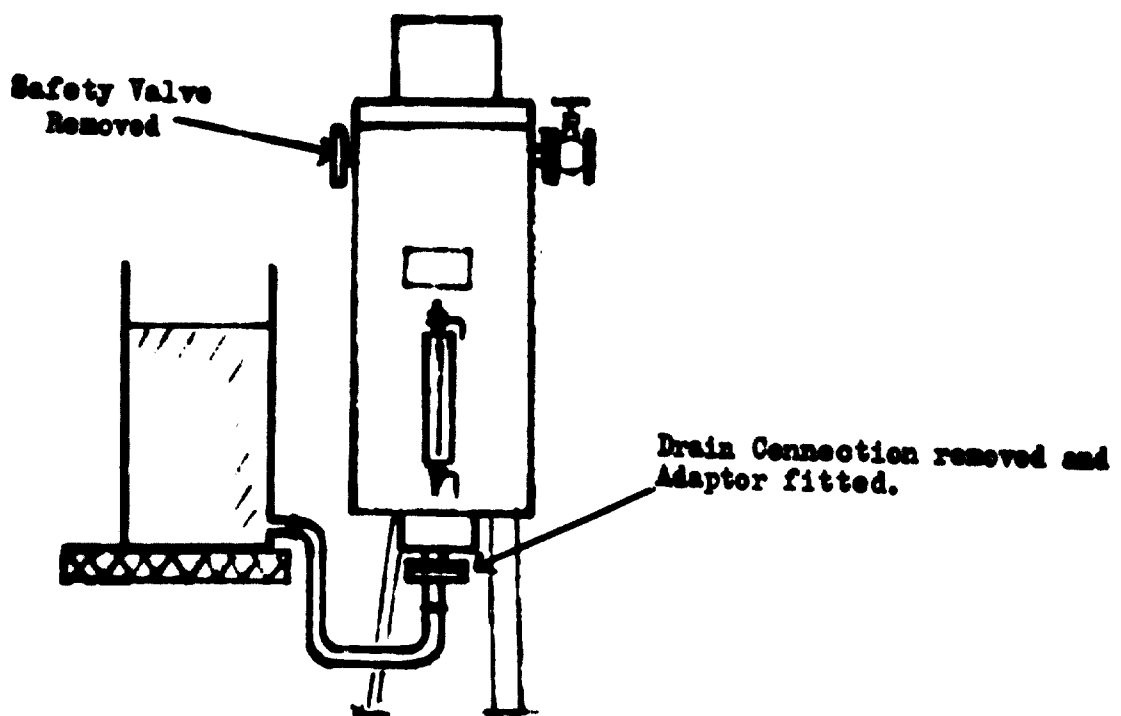Removed

Drain Connection removed and
Adaptor fitted.

Fig. 9.   Section 5.2.

'SIP & SOAK' CLEANING OF ELECTRODE BOILER.

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(i) Drain the unit. Remove safety valve to provide vent to atmosphere. Close gauge glass cocks.

(ii) Obtain a suitable tank with bottom outlet connections. (A cut down oil drum with a welded in spigot is suitable).

(iii) Connect the outlet of the tank to the blowdown drain of the unit (or any convenient branch near the bottom of the boiler). Rubber hose is suitable.

(iv) Place tank at a level so that the top of the tank is about three inches above the level of the upper gauge glass fitting of the boiler. See figure 9.

(v) Pour into the tank a solution made up of one part by volume of inhibited formic acid with fifteen parts of cold water. The solution will drain by gravity into the unit.

(vi) Continue adding solution until the height of liquid in the tank remains static at a point about level with the upper gauge glass fitting on the boiler.

(vii) Allow solution to remain in the unit for 16 - 24 hours then drain down, flush out thoroughly with cold water to remove any undissolved sludge and neutralise as described in paragraph 5.1.1. (xvii) after filling and draining several times with water.

(viii) Inspect unit, and if necessary, repeat process if deposits are too heavy to be removed in one application.

(ix) Reinstate connections and return unit to service.

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5.3. Precommission Cleaning of Fuel Oil Lines on Furnace.

Owing to the possibility of detached pieces of scale and rust causing choking of the small jets in oil burners, precommission cleaning of fuel oil systems is often employed. The following is an example of the progress of such a cleaning operation. The circuit was as shown in Figure 10.

(i) The system was filled with hot water which was available on the plant. Circulation was started via the pump.

(ii) Steam was injected into the steam side of the fuel oil heaters to raise the temperature to $95^{\circ}C.$, while still in circulation.

(iii) Heat was cut off, and inhibitor and wetting agent were added while circulating via the tank.

(iv) Citric acid solution was added slowly in order to give an initial concentration of about 4% w/w of acid.

(v) Ammonia was then added to raise the pH. value of the solution to about 3.5 units.

(vi) Circulation continued, with periodic testing of the solution for residual "free" citrates (i.e., that uncombined with iron). The following figures were obtained:-

	Total Citrate	Total Iron	"Free" Citrate
00.00 hours	4.10%	0.2%	3.42%
00.30 hours	3.92%	0.4%	3.06%
01.00 hours	3.84%	0.5%	2.14%
01.30 hours	3.78%	0.5%	2.10%
02.00 hours	3.74%	0.5%	2.01%
02.30 hours	3.71%	0.5%	2.01%
03.00 hours	3.71%	0.5%	2.01%

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Oil lines disconnected from
burners temporary byepass hoses
fitted.

Fuel oil heater in
circuit

Temporary return
lines

Line from tank
isolated

Permanent
Installation pump.
Isolated & byepassed

Chemical cleaning
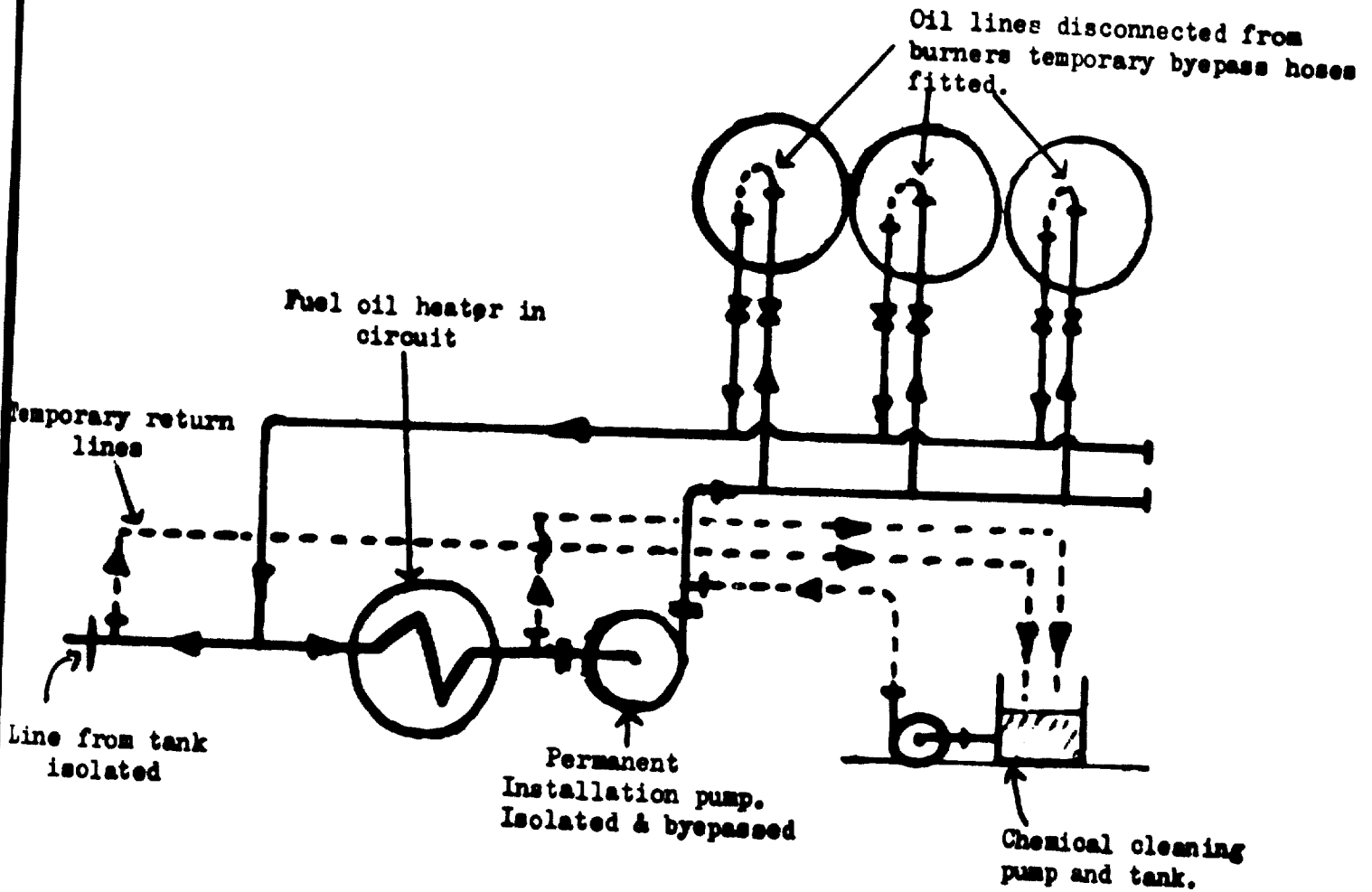pump and tank.

FIG. 10. SECTION 5.3.

PRECOMMISSION CLEANING OF FUEL OIL SYSTEM.

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(vii)   The results indicated the end of the process, so the unit was drained and flushed with a 0.1% solution of citric acid.

(viii) The system was purged with clean water at a rate sufficient to ensure a flow of 4' per second in the largest pipework, the circuit being flushed through all available points to remove solid debris.

(ix)   The system was passivated by circulating demineralised water containing 300 ppm of hydrazine and 50 ppm of ammonia, heated to 90°C. for 12 hours then draining. (This is a more sophisticated method of passivation often used in power plant cleaning.).

5.4 Vapour Degreasing of large vessel.

This method describes the use of trichlorethylene vapour to degrease a large vessel contaminated with oil.

The equipment is shown in Figure 11, together with the method of connection to the vessel.

The method relies on the fact that trichlorethylene vapour, (fed to the vessel from the vapouriser) condenses on the cool surfaces of the vessel and runs down.   The condensed solvent dissolves the oil film on the unit, returning this to the vapouriser.   Fresh solvent redistils continuously leaving the oil behind. As the unit warms up, the vapour level rises and eventually reaches the top of the unit - hence cleaning all surfaces.

This method is not satisfactory where heavy insoluble deposits are present together with the oil.   In such cases. degreasing with alkaline detergent mixtures is necessary.

When all contamination has been removed, the vapouriser is disconnected, all connections are removed, and the unit is blown out with air to remove all
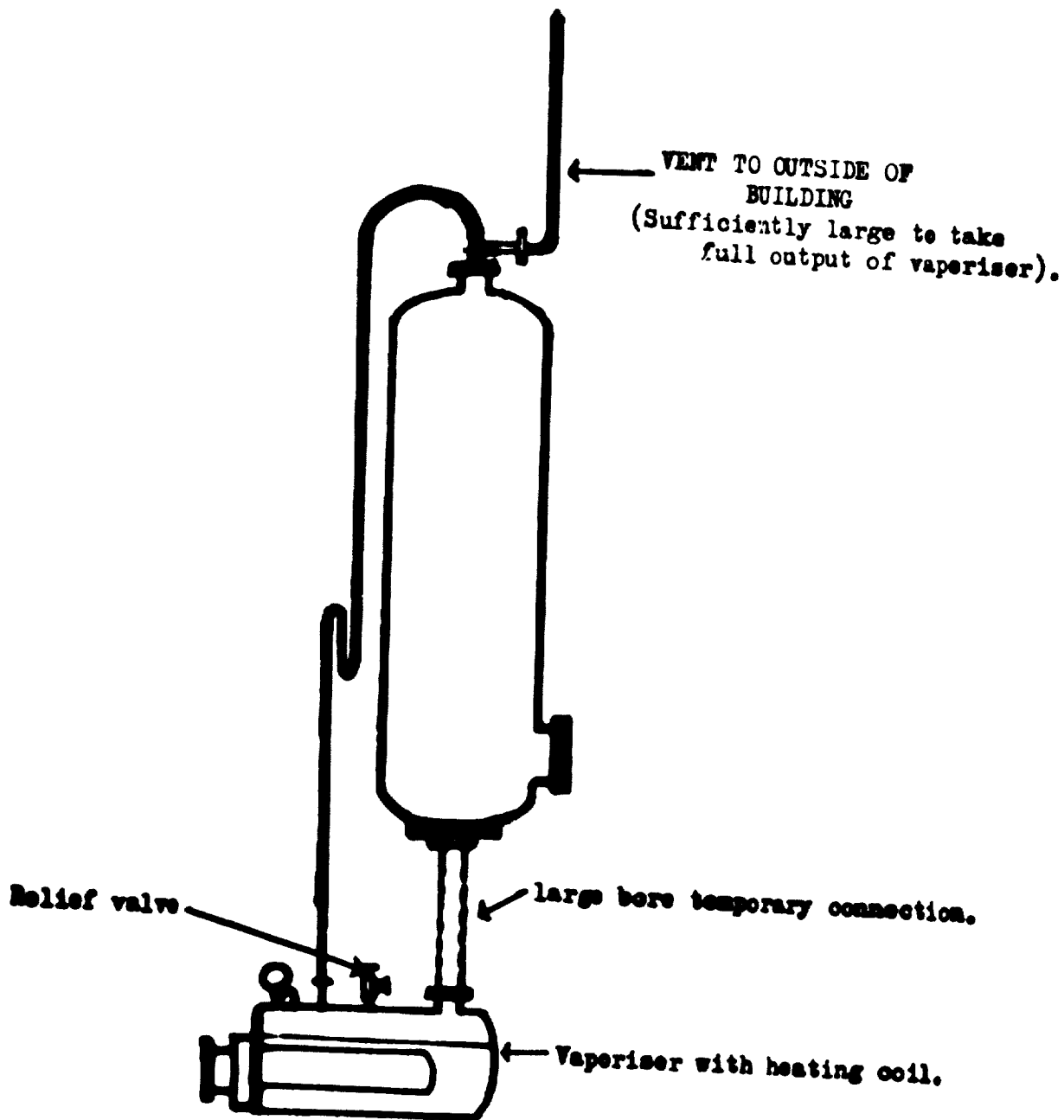
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VENT TO OUTSIDE OF
BUILDING
(Sufficiently large to take
full output of vaporiser).

Relief valve

large bore temporary connection.

Vaporiser with heating coil.

FIG. 11.   SECTION 5.4.

VAPOUR DEGREASING OF LARGE VESSEL.

gases.

N.B. Trichlorethylene vapour must be used with care, and the suppliers
of the solvent will advise on precautions to be taken when using
this.

5.5 Alkaline Degreasing of an Oil Cooler.

The problem, to remove oxidised oil deposits from the shell side
of an oil cooler as shown in Figure 12.

Method:

(i). Drain all oil from the unit.

(ii). Fill the unit with water in which has been dissolved a proprietary
degreasing mixture suitable for use in contact with materials of
constructions of the plant, at the concentration recommended by the
manufacturer.

(Alternatively, a mixture containing equal parts of caustic soda and
tridosium phosphate, together with about 2% of a synthetic surface
active agent is suitable for mild steel plant when used at up to 5%
concentration).

(iii). Heat the water by introducing steam into the unit, either via a drain
connection or by passing steam through the tubes.

(iv). Scum off the surface of the liquid by overflowing the solution from
the top branch - this removes surplus oil and economises in the use
of the cleaning chemicals. Continue heating.

(v). When no more oil can be scummed off, drain the unit.

(vi). Wash out thoroughly with water.

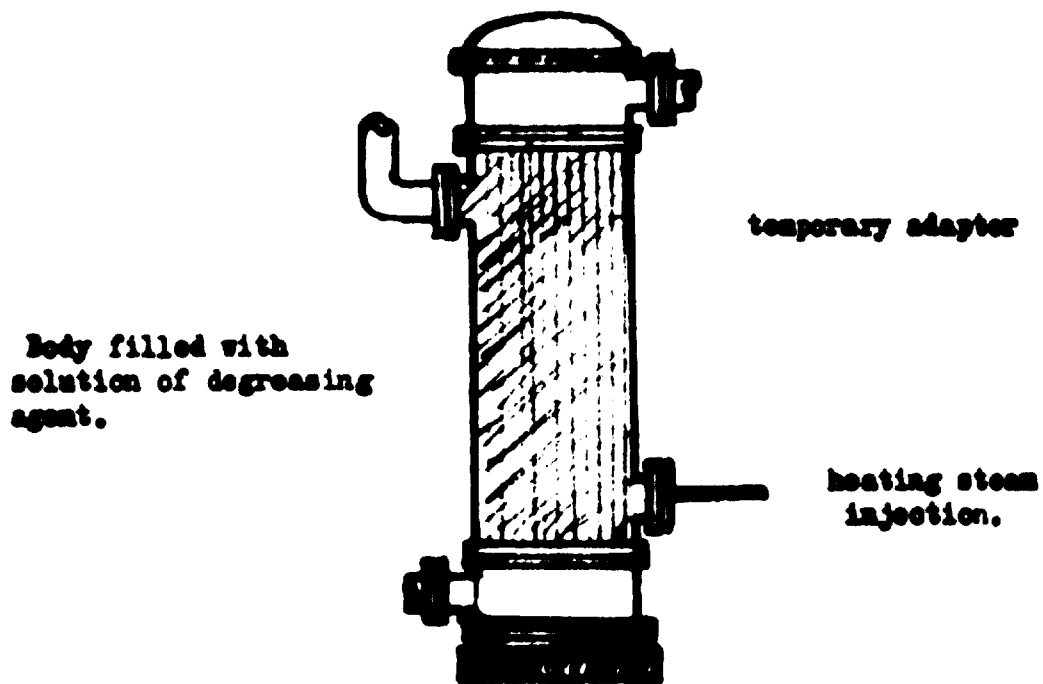(vii). Inspect and repeat if necessary.

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temporary adapter

Body filled with
solution of degreasing
agent.

heating steam
injection.

FIG. 12.   SECTION. 5.5

ALKALI DEGREASING OF OIL COOLER.

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5.6 **Chemical Cleaning of absorbtion column and gas coolers on nitric acid plant, using inhibited sulphamic acid.**

The use of sulphamic acid was necessary because of the variety of materials of construction present, which included austenitic stainless steels. The system was fouled with water hardness scale.

(i). The system was filled with water, and circulation established.

(ii). The system was inhibited by adding sufficient inhibitor for the circuit dissolved in a small quantity of acid solution, 500 lbs. of acid - 10 lbs. of inhibitor.

(iii) Acid injection then continued, the following results being obtained

Time	Acidity Residual	Total Amount of Acid added	Total Inhibitor added	Remarks.
13.30	Nil	500 lbs.	10 lbs.	Circulating
14.00	0.05N	1000 lbs.	20 lbs.	-do-
14.30	0.05N	1500 lbs.	25 lbs.	-do-
15.00	0.07N	2000 lbs.	27 lbs.	-do-
15.20	0.07N	2500 lbs.	30 lbs.	-do-
16.30	0.27N	4500 lbs.	110 lbs.	-do-
17.00	0.28N	-	-	-do-
17.30	0.32N	5200 lbs.	-	-do-
18.00	0.36N	-	-	-do-
18.30	0.38N	-	112 lbs.	-do-
19.00	0.38N	-	-	-do-
19.15	-	5500 lbs.	-	-do-
19.30	0.38N	-	-	Closed off No. 1 gas cooler.
20.15	0.38N	-	132 lbs.	Circulating
20.30	C.30N	-	-	Bad frothing, ceased adding acid.
21.30	0.4N	-	-	Circulating
22.00	0.4N	6750 lbs.	-	Circulating

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Time	Acidity Residual	Amount of Acid Added	Inhibitor added	Remarks.
22.30	0.4N	-	-	Circulating
23.00				Closed off valve on small exchanger to push acid up column.
01.30	Recommenced circulation, added remaining acid (total of 4 tons added to system).			
02.30	0.4N	4 tons	152 lbs.	Circulating
03.00	0.4N	-	-	-do-
03.30	0.4N	-	-	-do-
04.00	0.4N	-	-	-do-
05.00				Commenced draining system
07.00				System drained, commenced filling for first wash.
09.30				System full, commenced circulating.

TABLE 1.

DEPOSIT	CAST IRON ♦	MILD STEEL	COPPER ALLOYS	STAINLESS STEELS	ALUMINIUM LEAD TIN PLATING	CAD/NICKEL
CARBONATE HARDNESS SCALE	1 cold 10%w/▼ 4 cold 10%v/▼ 5 cold 10%m/■	1 cold **15%v/▼ 4 70°C. 10% ▼/ 5 70°C. 10% ■/▼	*** 1 cold 10%v/▼ 4 50°C.10%v/▼ 5 50°C.10%v/▼	5 70°C.10%m/■	4 70°C.10%v/▼ 5 70°C.10%m/■	4 Cold 10%m/▼ 5 Cold 10%m/■
IRON OXIDE (RUST ETC.)	1 cold 10%v/▼ 2 cold 5%v/▼	1 70°C. 15%v/▼ 2 60°C. 5% ▼/ 3 90°C.5.0%m/■	*** 1 cold 10%v/▼ 2 cold 5%v/▼ 3 90°C. 3%m/■	3 90°C. 3%m/■ (2)* 60°C.5%m/▼	3 (AMMONIATED) *****	-
WATER FORMED SLUDGES	1 cold 10%v/▼ 2 cold 5%v/▼	1 70°C. 15%m/▼ 2 60°C. 5%m/▼	*** 1 cold 10%v/▼ 2 cold 5%v/▼	5 ** 70°C. 10%m/▼ (2)**60°C. 5%m/▼	4 70°C.10%v/▼ 5 70°C.10%m/▼	4 cold 10%m/▼ 5 cold 10%m/■
CALCIUM PHOSPHATES (BOILER DEPOSITS).	1 cold 10%m/▼	1 70°C. 15%m/▼	*** 1 cold 10%v/▼	5 70°C. 10%m/■	-	-

1 - Inhibited hydrochloric acid
2 - " sulphuric acid
3 - " citric acid
4 - " formic acid
5 - " sulphamic.

* Cast iron is always attacked to some extent by inhibited acids.
** Hot solutions would foam too violently.
*** Plus dezincification additives for brasses.
**** Some authorities prohibit.
***** Consult contractor.
****** Attack unavoidable.

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6.0   **MANPOWER & TRAINING FOR CHEMICAL CLEANING.**

6.1   **What sort of people are needed?**

When chemical cleaning operations are examined, the work involved can be separated into three main sections:-

Design and planning of the cleaning operation

Mechanical preparation

Operation and control of the process.

If these sections are looked at further from the standpoint of personnel requirements, a broad picture of the type of people required in order to carry out the cleaning process is obtained.

6.1.1. Design & Planning.

This section will obviously include the person who has overall charge of the cleaning process.   His responsibilities will be:-

1. Having or acquiring a good working knowledge of the plant to be cleaned.

2. Being able to assess the most economical time to clean.

3. Deciding the type of process most suited for the operation.

4. Designing the circuiting necessary for carrying out the process.

5. Preparing a programme for the cleaning operation and liasing with other personnel so that this may be slotted in to reduce outage to the minimum.

6. Ensuring the safety of personnel and plant during the whole of the cleaning process.

7. Supervision of all stages of the operation to ensure maximum efficiency.

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8. **Arrange** all services required for the clean, water, heat, light, drainage.

From the above, it is seen that some specialized knowledge of chemical cleaning is necessary in this position. Items 1, 5 and 7 should be within the scope of any executive engineer or plant chemist, while the remaining sections are those requiring more detailed study.

Where the extent of chemical cleaning work is small, and the items of plant to be cleaned are not complex, it is probable that formal training is not necessary for the overall supervisor. Most chemical cleaning companies will act as consultants, and will be prepared to advise on the type of process and the circuitry required for chemical cleaning operations. The technical literature issued by such companies gives general guidance in carrying out the process. Furthermore, most reputable companies will be prepared to send technicians overseas in order to supervise chemical cleaning work. If, therefore, the extent of cleaning involves only a small amount of work, which may be carried out, say, annually, then it would obviously be economic to arrange that the first process was supervised by an expert from one of the companies in the field, during which a suitable engineer or plant chemist could be given the essential training to be able to repeat the operation.

My company has carried out chemical cleaning operations on the above basis in all parts of the World, including Italy, Portugal, Nigeria, Hongkong, Singapore, and still benefit from this in the sale of chemical cleaning materials.

Where chemical cleaning is used continuously, and where the plant

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is large enough to set up a separate chemical cleaning section, the
overall supervisor will, obviously, require a formal training in order
that he can design and carry out cleaning operations on a wide variety
of plant without having to enlist the aid of consultants on all
occasions.   Petroleum refineries are an example of the type of
industry where chemical cleaning is required frequently, and often
at very short notice.   Other large industries, particularly those
which have centralised control, such as the Electricity Generating
industry, will also fall into the category where separate chemical
cleaning services will be required.

If chemical cleaning contractors are available locally, it is
doubtful whether it is possible to carry out cleaning processes more
economically than they by the establishment of a central cleaning
service, since obviously the contractor will be working on maximum
deployment of his labour and equipment.   Where such services are not
available, then a self-contained section is the only answer.

Chemical cleaning is a relatively new science, and the literature
available is mostly in the form of short papers describing specific
cleaning operations.   While a great deal of information can be gathered
from these, it is probable that the difficulty in learning from them
would be the proverbial one of "not seeing the wood for the trees".
The only alternative for the training of overall supervisors would
therefore seem to lie in them spending a specific period with a
chemical cleaning contractor.   In selecting a candidate for such
training, his background education must obviously be studied closely.

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In general, the bias in chemical cleaning supervision is towards an engineering background, but with a strong leaning towards chemistry.   Much of the recruitment in the chemical cleaning contract field comes from the marine engineering group.   If separate chemical control of the process can be exercised, then the knowledge of chemistry required will be of a very basic nature.

Recently there has been a swing towards chemical engineers or even chemists as leaders of chemical cleaning teams, with a proviso that chemists should be of rather a practical leaning than purely academical. Plant chemists usually acquire this attitude and so are able to carry the responsibilities required.

Although the practice is not yet well established, it seems certain that training of supervisors for the developing countries by the reputable chemical cleaning contractors could become common.

The most obvious approach would be for the engineer or chemist to spend at least six months working with and for a cleaning contractor. Providing that the training programme is well planned, it should be possible within that time to absorb the principles behind the practical methods used.   Alternatively, it may be possible to arrange a period of training with one of the industries in the developed countries which use acid cleaning to a large extent within their organisation.   Examples of these would be the electricity generation authorities, refineries and similar industries with a centralised organisation.   In a large organis-ation of this nature, it should be possible to acquire a fairly

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concentrated period of acid cleaning experience, although that experience would be specific for one industry. It should be emphasised that the training should be mainly practical in nature. The basic chemistry involved is relatively uncomplicated provided that conditions are kept within the limits specified by the cleaning reagent manufacturers. A large part of the acid cleaning expertise is somewhat intuitive, and cannot be acquired from theoretical considerations alone.

The engineering aspects would be exhibited by following a chemical cleaning enquiry through from the initial survey, quotation, detailed survey, rigging, operation, inspection, and breaking down of the circulating plant.

One of the most important aspects of the training should certainly be the safety rules and regulations to be observed. Many of these are general for handling chemicals, but quite a few are specific to acid cleaning processes. It is obviously the responsibility of the supervisor to see that these rules are strictly observed, and this is one of the most difficult requirements of the job. The proper safety equipment must not only be available, but must be used.

A set of general safety rules for chemical cleaning operations appears at the end of this section.

6.1.2. Mechanical Preparation.

The requirements of the personnel engaged in this section of the chemical cleaning work are essentially those required of pipefitters in general. In the smallest operations envisaged, the connections are

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made using flexible hose with clips, and the actual fittings to the plant are made using simple adaptors, easily fabricated in the fitting shop.

On larger operations, steel flanged pipework usually replaces flexible hoses because of the greater safety factor. This pipework need not be of the same standard as normally used to construct plant, since obviously, it's only requirement is to remain leaktight during the progress of the clean. As an illustration of this, I arrived in one African country to carry out the chemical cleaning of a boiler unit, only to find that the whole of the pipework provided for temporary connections had gone astray. A replacement set was, however, made on the spot by the maintenance staff using old sections of replaced boiler tube fitted together with chequer-plate flanges. Soft rubber jointing was used to take up the inevitable gaps in joints. The clean proceeded without mishap to a successful conclusion.

No special training is necessary in this particular section - if anything a slight relaxation of general engineering standards is permissable so long as the safety of the operation is not involved.

6.1.3. Operation and Control.

While it is doubtless true that the success of any chemical cleaning operation lies in good design and planning, it is equally true to say that maloperation can just as quickly ruin it.

Once the mechanical preparations have been completed, the overall supervisor and his operators take over. The requirements of personnel in this section can be subdivided further as follows:-

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1. Those who operate the circulation and valving of the plant.

2. Those who control the chemistry.

3. The labour element.

In small operations, the boundaries between the subgroups would obviously become indistinct, but if we consider a fairly large cleaning process, the individual responsibilities and duties of these groups can be defined.

First and foremost, all employees falling within this group must have basic training in handling chemicals. They must understand the safety precautions and be prepared to abide by them. Training in these requirements is very basic, and should easily be achieved by the overall supervisor.

The operators should be capable of operating the pumping plant under non-ideal conditions and, should be of a sufficiently high level of intelligence to be able to operate control valves, injection pumps, mixing equipment etc., under direction They should furthermore be trained in the steps to be taken to minimise damage to the plant and possible injury to personnel in the event of spillage of chemical solutions.   It is essential to pull up leaking joints, pump glands and similar abominations quickly, and not to await the arrival of the pipefitters.

In general, the operators should have some experience in plant operation, and should be trained as a team by the supervisor.

The requirements for chemical control staff are not stringent if the supervisor is experienced.   The principal requirement is the

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ability to carry out site tests on the cleaning solution at frequent intervals, and to produce the results <u>quickly</u> with reasonable accuracy. The accent here is upon the word quickly. It is of no value in determining the progress and safety of the operation to produce very accurate results long after the acid has been drained. The principal requirements are for acid strength and iron concentration, the first to determine that sufficient reagent is present to complete the process, the second to confirm the absence of continued attack on the metal, both of them on reaching a stable level confirm the end of the cleaning process. Simple methods are adequate, titration for acidity and colormetric methods for iron, so no very high level of chemical achievement is necessary.

The requirements are thus well within the scope of a plant chemist and require no special training over and above that required for carrying out the day to day work.

To summarise, therefore, the necessity for formal training is restricted to one person, who should subsequently be able to pass on the essential knowledge required at lower levels. All must, however, be trained in safety precautions and first aid, for obvious reasons.

6.2.   <u>How Many People?</u>

One of the advantages which chemical cleaning has over mechanical methods is that the manpower required is considerably less for carrying out any specific task. For example, my Company has recently completed the chemical cleaning of the largest Nuclear Power Station in the World, prior to the commissioning of the plant. This operation which involved the treatment of

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the two nuclear reactor boiler units, each containing four separate boiler circuits, was carried out using a basic team of eight men and two supervisors. The circuits contained some 100,000 gallons of water, and temporary pipework was laid to connect the boiler units with the circulating pumps. The preliminary pipework erection was carried out by the team as a whole over a period of some five weeks, the process itself occupied the team for one week, during which time they were split into two shifts of four men and one supervisor, and the final breaking away of the pipework occupied a further two weeks. Similarly, the turbine feed and condensate systems on the same power station were cleaned using the same labour force. Quite apart from the fact that mechanical methods could not achieve results which were obtained by chemical cleaning, the manpower involved to clean some 10,000 intricate tube sections in the boiler units by mechanical means would have far exceeded that used for the chemical process.

Where the cleaning of, for example, a small heat exchanger is involved, the manpower required is usually only two men. My Company, again in this field, operate on a two man-team basis, the whole of the equipment being taken to site in a light van, the men connecting the flexible pipework to the unit to be cleaned, the acid being introduced on the first day, and the subsequent washing out and final treatment being completed on the second day. It is, of course, possible when actually working on the site to complete the chemical cleaning during a single day.

It is relatively easy to economise on manpower in this respect by good planning of the chemical cleaning process. In the larger operations, it is obviously advantageous to use chemicals in bulk, and to handle these

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by pumping directly from storage tanks into the cleaning circuit. Where smaller units are involved, labour saving devices such as carboy emptying pumps have been recommended previously, and will cut down considerably in man hours involved in carrying out the cleaning process.

6.3. THE HAZARDS OF CHEMICAL CLEANING.

6.3.1. Personal Protection.

The most obvious hazard in chemical cleaning processes is that resulting from handling the materials themselves. These materials are usually corrosive towards the skin, e.g., mineral acids or alkalis, and the usual precautions must be adopted when handling them. Gloves and goggles are essential, and some form of overall protection is obviously desirable. Protective aprons and sleeves are useful in that they reduce the amount of damage to overalls by corrosive liquids.

Where exceptionally corrosive materials are being handled, full protective clothing must be worn.

The main problem in ensuring that workmen employed in carrying out the chemical cleaning processes are fully protected lies in the difficulty of overcoming the reluctance to wear protective clothing. It is, however, the duty of management to see that such protective clothing is available and is worn. Where harmful vapours are present, suitable respirators or positive pressure breathing apparatus must be worn, even though these are uncomfortable particularly in hot climates.

6.3.2. Hazards Arising from the Process.

The process itself must be carefully examined to ensure that no hazards arise as a result of the chemical reactions taking place within the plant.

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Where, for instance, carbonate deposits are being dissolved, large quantities of carbon dioxide are produced and good ventilation must be ensured in order to avoid any pockets of this gas from collecting in circumstances which may eventually prove dangerous.

It should always be borne in mind that a limited amount of attack on the parent metal always takes place when inhibited acids are being used. This means that when acid cleaning solutions are drained from a plant or vessel, the space inside may often contain sufficient hydrogen to produce a serious explosion if naked lights are allowed near the plant at this stage. It is thus essential that <u>no smoking or naked lights are allowed in the vicinity of a chemical cleaning process</u> until the equipment can be proved to be completely gas-free. This is a most real hazard.

SAFETY RULES FOR OPERATORS ENGAGED IN CHEMICAL CLEANING PROCESSES.

1. WEAR THE PROPER PROTECTIVE CLOTHING AND EQUIPMENT.

2. TREAT <u>ALL</u> MATERIALS AS HARMFUL, DON'T TOUCH CHEMICALS OR RESIDUES WITH BARE HANDS. WASH AWAY ACCIDENTIAL CONTACT IMMEDIATELY.

3. KEEP YOURSELF AND YOUR CLOTHES CLEAN. REMOVE AND WASH CONTAMINATED CLOTHING BEFORE RE-USE.

4. WASH AFTER HANDLING CHEMICALS - DON'T EAT, DRINK OR SMOKE UNTIL YOU HAVE.

5. ENSURE SAFETY OF OTHERS BY WARNINGS AND BARRIERS WHERE NECESSARY.

6. VENTILATE AREA OF PLANT BEING CLEANED. CLEANING PROCESSES MAY EVOLVE INFLAMMABLE, SUFFOCATING OR POISONOUS GASES. SPECIAL VENTILATION IS REQUIRED BEFORE ENTERING PLANT FOR INSPECTION PURPOSES. WATCH FOR OBVIOUS GAS POCKETS (LIGHT OR HEAVY GASES).

7. DON'T SMOKE OR USE NAKED LIGHTS ANYWHERE NEAR PLANT WHICH IS BEING CLEANED AT ANY STAGE OF THE PROCESS.

8. READ AND UNDERSTAND THE SAFETY PRECAUTIONS CONCERNING HANDLING OF MATERIALS.

9. IF IN DOUBT, ENQUIRE WHETHER YOUR JOB PRESENTS ANY SPECIAL HAZARD.

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10. OBEY SPECIFIC INSTRUCTIONS CONCERNING CLEANING PROCESSES. MIX CHEMICALS ONLY IN ORDER SPECIFIED.

11. WASH AWAY AND NEUTRALIZE WHERE NECESSARY ACCIDENTAL SPILLAGE OF CHEMICALS OR CLEANING SOLUTIONS. DO NOT ALLOW SPILLAGE TO DRY OUT.

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7.0   ## IS CHEMICAL CLEANING FEASIBLE IN THE DEVELOPING COUNTRIES?

One of the major problems facing any chemical cleaning contractor
is the recruitment and training of suitable operators.   In the case of
a process plant operator, however, it is necessary to have a maintenance
staff composed of artisans of one class or another.   In this respect,
therefore, the plant operator has a nucleus of personnel who are of
sufficiently intelligent calibre to be able to carry out chemical cleaning
processes, provided that suitable trained supervision is available.   A
separate section has emphasised the necessity for ensuring that such
supervision has a good basic training in chemical cleaning methods, and it
must be emphasised that any attempts to carry out anything other than simple
chemical cleaning processes without such supervision is to be discouraged.

A factor which must not be overlooked, particularly in respect of
pressure plant such as boilers, is the necessity for ensuring that plant
insurance is not jeopardized by carrying out   chemical cleaning processes
by unskilled personnel.   In the United Kingdom, the chemical cleaning contract-
ors carry insurances indemnifying the Companies against claims of around a
million pounds, and these insurances are, of course, only issued on the basis
of a firm understanding between the contractor and the insurer who, obviously,
requires evidence that the technical standing of the contractor is good.
Boiler Inspectors in general in the past have been somewhat reluctant to accept
acid cleaning, but they now, in fact, as a body, recommend it.   There is little
doubt, however, that the plant operator would obtain the blessing of the
Insurance Company providing that the method has been recommended by a reputable

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chemical cleaning contractor, especially if the supervisors of the process had received training from such a contractor.

A separate section of this paper has reviewed the type of equipment which must be used for the cleaning process. It must be evident from this, that equipment for carrying out a simple chemical cleaning process will usually be available where industrial development has been taking place. From the foregoing, therefore, it is obvious that the only possible limitation on the feasibility of chemical cleaning in the developing countries lies with the availability or otherwise of the basic raw materials needed for the process.

7.1 The Availability of Chemical Cleaning Materials in developing Countries.

In recent years, the chemical cleaning Companies have realised the potential of the market in the developing countries. In most cases, however, such countries are supplied with made-up chemicals usually available only by export from the developed areas. In only a very few cases are the made-up materials being manufactured in the developing countries, but it is undoubtedly only a matter of time before such materials are made under licence throughout the World. In the meantime, however, the major problem is the acquisition of such made-up chemicals which usually involves carrying rather large stocks which are obtained by import from the developed countries.

This method, of course, does have the advantage that the experience of the manufacturing Company can be drawn upon freely in obtaining these chemicals, but has obvious disadvantages in the high cost of import of such materials.

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Since the bulk of the materials used in chemical cleaning is undoubtedly inhibited acid, it is an obvious proposition to consider the import of the inhibitor materials alone. As has been shown previously, nowadays such inhibitors are rather complex products which are usually unobtainable except in the highly developed countries. It is, however, usually possible to obtain the basic acids in those areas of the World which are at present developing industrially.

The most important material is, without doubt, hydrochloric acid, and this is becoming much more freely available throughout the World particularly where petroleum refining is carried out. The other basic materials usually used in simple chemical cleaning processes are as follows:-

hydrochloric acid commercial specific gravity 1.14 to 1.18

sulphuric acid C.O.V.

sulphamic acid technical

citric acid, anhydrous, monohydrate or 50% solution of monohydrate

caustic soda, powder, pellet, flake or solution

trisodium phosphate anhydrous or crystalline

nonionic detergents

anionic detergents

The less important chemicals, but those which are used to some extent in quite common chemical cleaning methods are as follows:-

nitric acid commercial

hydrofluoric acid commercial

formic acid commercial

sodium fluoride

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ammonium bifluoride

sodium metasilicate

soda ash

It is, of course, much more profitable for the chemical cleaning manufacturer to export a finished product for use overseas. Economically, however, this is not sound, and the solution probably lies in the fact that the chemical cleaning Companies will make their experience freely available on the basis of acting as consultants to the process plant operators. In this way, the plant operators in the developing Companies get the benefit of the long experience behind the chemical cleaning contractor operating in the industrial countries of the Western World.

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