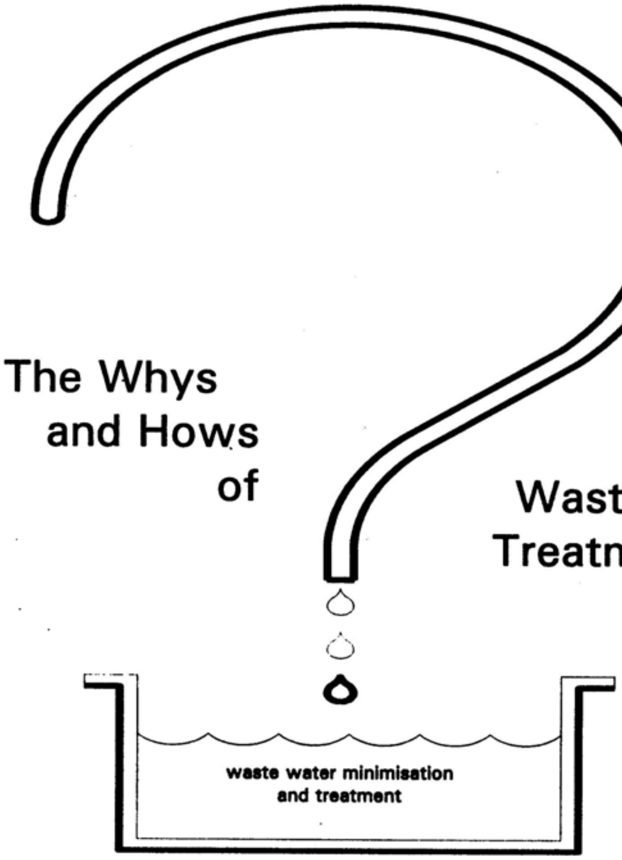
The Whys and Hows of Waste Water Treatment For Picklers



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1.0 **Why is Waste Water Treatment Needed ?**

Unless you have a totally effluent free pickling system (which is possible on some lines with today's technology, ask ESCO) then you need to get rid of rinse water, spillage and scrubber water and if you have them, lime and permanganate. All of the above are contaminants no longer acceptable in the environment without proper treatment although the byproduct sludge from the treatment plant is not considered hazardous.

All other chemicals used as coatings after pickling such as zinc stearate and zinc phosphate and neutralizers for phosphate coatings (borax) are considered hazardous wastes because they contain heavy metals (zinc), but they can be treated. However, the sludge byproduct from the treatment plant then becomes hazardous waste. **Oily wastes are never acceptable in a waste water treatment system.**

The waters leaving these systems all contain dissolved metals and acid. Both are contaminants, toxic or not and need to be separated from the water before it can be discharged to sewer or waterways.

1.1. Waste Generation.

There are basically two separate categories of picklers:

Steel picklers and **alloy** picklers (includes titanium)

The source of waste generation is the same on both but the composition of the waste is different. Therefore the treatment of the waste is also different. We will concentrate on the steel picklers in this booklet for explanatory reasons, because the basic principles of treatment apply to alloy picklers also; only the chemistry is different and slightly more complicated. Alloy picklers are invited to contact ESCO for information pertaining to their operations.

1.1.1. Rinse Water

Every pickling system has a rinse section to remove residual pickling acid from the pickled steel by using water. The majority of waste water is created here.

A lot of treatment costs can be eliminated by having effective low water rinse systems and using rinse water for makeup in the pickle tanks for evaporation and dragout losses. This is a first step toward recycling and should be practiced religiously.

1.1.2. Scrubber Water

Every pickling system except a fumeless pickler has a fume exhaust system to control escape of unwanted fumes from the pickle tanks and related equipment. The fumes are controlled by air streams drawn through the equipment openings. Before this air can be discharged to atmosphere the evaporated or entrained acids, which also contain dissolved iron, must be removed.

This is done by fume scrubbers using water as a scrubbing medium. The resulting waste water is a second source of waste to be treated. Again here as in rinsing, practice conservation and recycling. This waste water can also be returned to the pickle tanks if the scrubbers are of the type needing very little water.

If reuse is not possible, then the scrubber water should be combined with the rinse water flowing to the treatment system.

1.1.3. Lime Tank Overflow

Picklers that use a lime dip for coating invariably use live steam to heat the lime tank. This builds up condensate in the lime tank and causes the lime tank to overflow continuously. Because lime is a chemical that can be used to neutralize acid, it is advantageous to overflow this tank into the waste water stream to be treated.

Here also conservation can be practiced by only overflowing clear lime water and not the lime suspension. This can be accomplished by underflowing into the overflow tube allowing the suspended lime to settle in the tube before it gets to the overflow level.

1.1.4. Caustic Permanganate (Potassium Permanganate With Caustic Added)

This chemical is used for desmutting pickled product. It is a very expensive material and normally is not allowed to overflow. The tank always had a closed heater so that no condensate will enter the solution. This causes evaporation from the tank and water needs to be added periodically.

This creates no continuous waste generation but the tank needs to be blown down once in a while to get rid of accumulated smut. The blow down must be mixed with pickle acid before it can be discharged to the treatment facility. The purple color disappears as soon as it comes into contact with the dissolved metals in the pickle acid.

1.1.5. Sumps, Spillage

Without fail picklers always have pits or containments with sump pumps for catching spills and wash down water. These sumps are a great catchall for gloves, cigarette boxes and butts, rags and whatever someone believes to be garbage. Also found in sumps and pits are oily wastes such as hydraulic fluid and lubricants. You must remember that the solution collected in the sumps eventually has to go through pumps and treatment equipment which are **not designed to be oil refineries or junk garborators**.

For this reason all containment areas and sumps must be kept clear of anything but water-based liquids and soluble solids. It is also important, to separate spillage areas which house hazardous materials from those that are non-hazardous to prevent cross contamination.

It is to the operators advantage to **get competent technological advice as to what can be treated and how, before any liquid waste is diverted to a waste water treatment plant.**

2.0. How Much Water Needs Treating?

Before you get involved in deciding whether or not to install waste water treatment or improving an existing waste water treatment system, ask yourself one question:

Do we really need to use that volume of water?

If this question can be answered with 'no, not really' you are on the way to substantial savings in treatment and/or hauling costs. Every gallon of waste generated in excess of what is really needed, increases the cost of hauling and treatment and therefore increases the cost of pickling per ton of product.

2.1. Water, Water Everywhere And Not A Drop To Waste!

As mentioned several times in chapter one, think the 3 R's when answering the question: how much water needs to be treated?

Reduce -- Reuse -- Recycle

2.1.1. Reduce

In most pickling systems we get involved in we always find that water is being used to the extreme, i.e. it's always "plenty" instead of "just enough". There are many ways to reduce water going to waste. For instance:

Do you leave hoses running just because you are too busy to shut it off when you are done with it?-- *3 gpm = 180 gph = enough to rinse 60 tons of steel coil!*

Do you have eye wash fountains or safety showers running steady to keep the rust out ? *-- 0.5 gpm = 720 gpd = enough to rinse 240 tons of steel coil.*

Do you have drinking fountains running steady to keep the water cool?

Do you use Niagara Falls forever to rinse your product just because there was a stain on it 6 months ago? (probably caused by using too much water to start with).

Do you flood your scrubber just because someone years ago found spots on a parked car? (probably caused by no water on the scrubber at all, at that time).

Do you hose down your equipment using a fire hose?

----------- and then wonder why your hauling costs are so high or why the treatment plant was "undersized"?

All of the water flows mentioned above eventually end up as waste water unless they are separated:

Eye wash and drinking fountains and safety showers discharge clean water and can be diverted out of the waste water areas. Even the hose; if you must run it don't run it into the waste water stream.

In the case of rinsing and fume scrubbing, there is technology in place today to accomplish better results by generating less waste water.

These are just a few examples of how waste water generation can be reduced. Take a walk around your pickle house thinking only --reduce-- and you will be amazed at what you will find that can be cut back.

Why all this talk about cutting back?---- only one reason:

The size of equipment needed in a waste water treatment system is based on gallons per minute to be treated not the amount of contaminants in those gallons.

2.1.2. Reuse

If you can make your water work two or three times before it needs treatment, you have cut the volume to be treated by as much. It is very easy to find uses for waste water if you have an up to date flow diagram of your facility. For instance:

There is no need to use clean water for evaporation makeup!

There is no need to use clean water to wash down spills!

There is no need to use clean water to hose out a pickle tank!

There is no need to use clean water to make up a new pickle tank!

This list can go on and on as you see fit or as the process allows. When using waste water over again remember what contaminants are in it and use it only where those contaminants can do no harm.

For example, do not use phosphate rinse water to make up a pickle tank - it will add zinc to the pickle acid which will make the spent acid more expensive to dispose of or treat, and will also contaminate the pickle rinse water treatment plant sludge.

Besides reducing waste water flows, recycling can reduce chemical losses by returning some of the drag-out to the process tank.

Just remember, **nothing needs to be started pristine clean in a pickling system because it gets contaminated again within the first 2 seconds of use.**

2.1.3. Recycle

When you are reusing waste water, in most cases, you are already recycling. For instance:

Reusing waste water for tank make up and evaporation loss returns the contaminants back to where they came from to start with. That's recycling. Again, remember what the contaminants are in the waste water and only recycle it to where those contaminants belong.

Recycling can be a tremendous cost cutter if the pickling system is redesigned to use up waste water. For instance:

If the heat and mass balance of the system are rearranged to make use of waste water, then by creating more evaporation in the pickle tanks more waste water can be recycled, means less needs to be treated.

2.1.4. How To Go About Cutting Back

Usually we find that the people involved with the operation of a pickling process are so busy trying to keep the tonnage up that a lot of minor details such as saving water and subsequently saving operating costs are being overlooked or there is just no time available to work on it.

In cases like that we highly recommend that outside engineering companies, familiar with the pickling industry, be consulted. These consultants will look into all aspects of possibilities for improvements in the entire system without being influenced by in-house policies and inherited bad habits. In other words you will get a fresh look at the forest by seeing the trees.

ESCO Engineering is such a company who has been involved in dozens of pickling systems over many years all over the world. In our experience, in most cases, the cost of documenting existing systems and then re-engineering them to recommend improvements and finally implementing those improvements is offset many fold by the savings realized. (See back cover for other publications by ESCO)

3.0. **The Pickling System** (as opposed to the pickle house)

In the above discussions "pickling system" or "the entire system" is mentioned quite often. The reason for this is that a pickle house or pickle line and a waste water treatment plant are not two separate processes; they must be considered as one pickling system and operated as such.

As you can see from the above many operations carried out on the pickle line heavily affect the operation and equipment choices in the waste water treatment plant. It is therefore very important that the two are looked upon as a one system operation with each relying heavily on the other for maximum efficiency. This must be kept in mind when designing improvements to existing or new facilities.

4.0 **Bread And Butter** (A look at some costs and savings by doing the right thing)

Here are some specific examples of savings made by applying the principles described in chapters 2 and 3.

4.1 Reduce

A stainless steel strip pickler was using 1100 gpm of river water for rinsing and scrubbing and discharging this water untreated into a river. New regulations required this water to be treated before discharge.

The volume of rinse water to be treated was reduced to 120 gpm by installing:

- countercurrent spray rinses
- low water consumption plate fume scrubbers

thereby reducing the capital cost of the waste treatment plant by 75%. In addition, the new rinses and scrubbers reduced acid losses and treatment costs, and improved product quality.

4.2 Re-use

A new copper rod plant was designed to generate 60 gpm of rinse water after pickling. By modifying the process to use a multi-stage rinse, and increasing the evaporative capacity of the fume scrubber, the rinse effluent was reduced to zero, so that the entire cost of a waste treatment system was saved. In addition, over $60,000/year of copper was returned to the pickle tank for recovery.

4.3 Recycle

A rod coil pickler was having continuous problems with overloading of the waste treatment system, and the pickle line was having to shut down at intervals to allow the waste treatment plant to “catch up”.

By revamping the rinse system to make better use of the water, and recycling rinse water to the pickle tank, the volume of effluent was reduced to about half the waste treatment plant capacity, so that production slow downs were no longer needed. Plant throughput was increased by 25% and acid consumption reduced by 10% due to recovery of acid in the rinse water.

5.0. **What is Waste Water Treatment For Picklers**?

Waste water from picklers contains acids and dissolved iron. The dissolved iron is actually in the form of iron salt just as cooking salt is a metal salt (sodium is a metal). As long as the iron salt is in the presence of acids, it is dissolved in the water.

Environmental authorities therefore have instituted regulations as to what type of solids are acceptable for disposal and which are not, together with limits as to the quantities allowable in the treated effluent water. This is mainly to prevent small volumes of hazardous material from contaminating large volumes of nonhazardous material.

In other words the onus is on the producer of relatively small quantities of waste to separate the potentially hazardous material before it enters publicly controlled streams. The process that can do this is called neutralization. The acid and iron salts are neutralized so that good can be separated from the bad.

This is in fact the waste water treatment process in a nut shell:

Making undisposable waste into disposable waste

by changing the chemical and physical conditions of the contaminants so that they can be separated from the water. **Nothing is destroyed** - what came in must go out, but in different physical and chemical form.

As you can see there are two separate items to be disposed of: water and solids (normally referred to as 'sludge'). The water is clean enough to go to sewer, but the sludge needs to be hauled away. Depending on the type of pickling being done, this sludge can be taken to a regular landfill as acceptable waste or, if it contains heavy metal, it must be taken to a controlled landfill as hazardous waste

As mentioned above hauling waste is a major cost if you do not have a treatment plant. Now here we are using a treatment plant, but we still need to haul stuff away?

Yes, that is a fact, but the amount being hauled away is so much less in volume, that it represents but a fraction of the cost of hauling all the liquid waste. In fact the process is designed to make sure that the sludge is as dry as possible before it is transported.

As can be seen from the above discussions, there is more to this than meets the eye and better explanations are necessary in order to understand the process. To comprehend all this better basic knowledge of the chemistry involved goes a long way. Do not worry, you need not be a chemist to understand the following chapter!

6. <u>The Chemistry of Waste Water Treatment</u>

6.1 <u>Basic Chemistry We Should Know About</u>

In order to understand the chemical waste treatment process, we must understand a few basic facts about related chemistry.

6.1.1 *<u>A chemical reaction</u>* is a happening where two chemically different materials combine to form one or more materials chemically different from the originals.

For example:
wood and air burn to form carbon dioxide and water
or in chemical terms

$$\text{hydro carbon} + \text{oxygen} \xrightarrow{\text{forms}} \text{carbon dioxide and water}$$

6.1.2 *<u>A physical change</u>* (as opposed to a chemical reaction) is a happening where only the form of the material is changed, as from its solid state to its liquid state, or vice versa, without changing its chemical make up.

For example:

heating ice to make water

6.1.3 *All matter on earth is made up of atoms* of basic elements combined in molecules to form compounds.

For example:

water is a molecule made up of two hydrogen atoms and one oxygen atom (H_2O).

6.1.4 *All atoms have been named* arbitrarily by scientists over many centuries and the short form of these names is commonly used to express chemical compounds.

For example:

H = Hydrogen
Cl = Chlorine
Fe = Ferrum = iron
O = Oxygen

6.1.5 *All atoms have atomic specific weights* based on hydrogen being 1. When combined into molecules, the sum of the weights of the atoms in the molecule is called the molecular weight.

For example:

water = H_2O = 2 hydrogen = 2 atomic weights
\+ 1 oxygen = 16 atomic weights
molecular weight of water = 18

This means that the water molecule is 18 times heavier than the hydrogen atom.

Atomic weights are listed in the periodic table of elements (figure 1). The following are those needed in the chemistry of pickling :

	Atomic Weight
H = Hydrogen	1
Cl = Chlorine	35.5
Fe = Ferrum = iron	56
O = Oxygen	16
Na = Sodium	23
Ca = Calcium	40
Mg = Magnesium	24
etc.	

6.1.6 *Atoms combine with each other only in specific ratios* to form molecules. These ratios were determined through experiments in science over many centuries. The reasons for these ratios are explainable, but the fact that they exist is all we need to understand at the moment.

For example:

water is always made up of 2 hydrogen atoms plus 1 oxygen atom

H_2O

it is never found as H_4O or HO_2 etc.

Molecules of specific atom ratios as they appear in the chemistry of waste treatment are:

Figure 1 - periodic table of elements

hydrogen chloride = HCl (one H + one Cl)
scale (iron oxide) = FeO (one Fe + one O)
ferrous chloride = $FeCl_2$ (one Fe + two Cl)
water = H_2O (two H + one O)
hydrogen = H_2 (one H + one H)
calcium hydroxide (lime) = $Ca(OH)_2$ (one Ca + two O + two H)
sodium hydroxide (caustic) = $NaOH$ (one Na + one O + one H)
sodium chloride (table salt) = $NaCl$ (one Na + one Cl)
magnesium hydroxide (magnesia) = $Mg(OH)_2$ (one Mg + two O + two H)

6.1.7 _Reactions are expressed in chemical equations_. As in mathematical equations, they must also balance: the number of atoms on one side of the equation must equal the number of atoms on the other side.

For example:

$$\text{iron oxide + hydrogen chloride} \overset{\text{makes}}{\rightarrow\rightarrow} \text{ferrous chloride + water}$$

From the discussion in 6.1.6 above, we know how many atoms are in each of the above compounds:

$$FeO + HCl \rightarrow\rightarrow FeCl_2 + H_2O$$

We now have an imbalance because there is one hydrogen and one chlorine too many on the right. The number of atoms alone cannot be increased on the left or decreased on the right because as we know, they only come in specific ratios.

However, we can change the number of molecules and thus create a balance, without disturbing the atomic ratio:

$$FeO + 2HCl \rightarrow\rightarrow FeCl_2 + H_2O$$

Now we have two hydrogen and two chlorine atoms on both sides on the equation. The equation is in balance, meaning that one molecule of scale will react with two molecules of hydrogen chloride to form one molecule of ferrous chloride and one molecule of water (pickling reaction).

6.1.8 _Molecular Weights Are Also In Balance_

For example:

the unbalanced equation as in 6.1.7 above would be expressed in atomic weights thus:

FeO + HCl	$\rightarrow\rightarrow$	$FeCl_2$ + H_2O
(56 + 16) + (1 + 35.5)	=	(56 + 71) + (2 + 16)
total 108.5	(not equal)	total 145

After it is balanced by molecules, the atomic weights balance also:

FeO + $2HCl$	$\rightarrow\rightarrow$	$FeCl_2$ + H_2O
(56 + 16) + 2x(1 + 35.5)	=	(56 + 71) + (2 + 16)
total 145	(balanced)	total 145

expressed in molecular weights (sum of atomic weights in each molecule)

$$FeO + 2\,HCl \quad \rightarrow\rightarrow \quad FeCl_2 + H_2O$$
$$72 + 73 \quad = \quad 127 + 18$$

6.1.9 Since _molecular weights are an indication of the weight ratio_ by which molecules will react with one another, it follows that by substituting the molecular weight numbers with weight units, we can thus calculate the mass required of each component taking part in a reaction. We can balance the actual mass of material, meaning we can do a MASS BALANCE.

For example:

in the balanced equation (or formula) in 6.1.8 above, we can see that by substituting the weight unit 'pound' with the molecular weight, it will take

72 lbs of iron oxide reacting with 73 lbs of hydrogen chloride
to make
127 lbs of ferrous chloride and 18 lbs of water

We started with 145 lbs of material and made 145 lbs of product.

6.1.10 Because _molecules are present on this earth in various physical forms,_ reactions must take place in an environment common to each molecule within the reaction.

For example:

looking at the physical forms of the components in the reaction in 6.1.9 above we can see that under ambient conditions:

iron oxide	is in SOLID form
hydrogen chloride	is in GAS form
ferrous chloride	is in SOLID form
water	is in LIQUID form

Since iron oxide dissolves in acid and hydrogen chloride dissolves in water to form acid, and ferrous chloride dissolves in water, it stands to reason that this reaction should take place in water as a common solvent.

The solvent water takes no part in the reaction itself; it merely provides a medium for the reaction to take place in.

This means that the amount of solvent water used at the start of the reaction is exactly the same as that at the end of the reaction, provided no physical change such as evaporation had taken place.

6.2 Chemical Reactions In Waste Treatment

When rinse water is neutralised, two reactions take place:

6.2.1 _Acid is neutralized_ (using hydrochloric acid as an example)

$$HCl + NaOH = NaCl + H_2O$$
$$\text{acid} + \text{caustic} = \text{table salt} + \text{water}$$
$$36.5 + 40 = 58.5 + 18$$
$$76.5 = 76.5$$

6.2.2 *Metal Salts are neutralized* (using ferrous chloride as example)

$FeCl_2$ + 2NaOH = 2NaCl + $Fe(OH)_2$
iron salt + caustic = table salt + iron hydroxide
127 + 80 = 117 + 90
207 = 207

6.2.3. *Iron Hydroxide is oxidized*

When the pH becomes alkaline (about 7), the green ferrous hydroxide is easily oxidized by the oxygen in the air to form brown ferric hydroxide

4 $Fe(OH)_2$ + 2 H_2O + O_2 = $4Fe(OH)_3$
ferrous hydroxide water oxygen ferric hydroxide
360 + 36 32 = 428

6.2.4 *Some Facts of Interest*

Both of the above reactions take place in solvent water. The water takes no part in the reactions, it only acts as a medium for the reactions to take place in. There is a small amount of water being created by neutralizing acid which simply mixes with the solvent water.

Note that both reactions make sodium chloride as a byproduct which is of course dissolved in the water. This means that the effluent water is actually salt water. This is why it is not a good idea to recycle the effluent water through the pickling system, although it could be used for such things as washing floors or hosing down equipment but is not recommended. Salt water is an acceptable waste in sewer streams.

Waste water is very acidic because of its acid content. The addition of basic material (neutralizers) such as caustic causes the reactions to take place. The change from dissolved salts to insoluble solid takes place when the solution changes from being acidic to being basic at a very narrow range between the two; too small to detect by conventional analysis methods. Yet in order to control these changes, we must know exactly at what level of acidity or basisity the solution is at. This is done by pH measurement which is described in section 9, 'Process Control'.

6.2.5 *Other Neutralizing Chemicals*

In the above examples caustic is used as a neutralizer. This is the most common and easiest chemical to use. However it is quite costly, presents a safety hazard, makes thin sludge and in certain applications not necessarily the best to use. The following are some other neutralizing chemicals commonly used:

Lime = calcium hydroxide = $Ca(OH)_2$
it is cheapest, precipitates sulfates and fluorides, makes denser sludge, relatively safe to handle, reacts reasonably quickly

Magnesium hydroxide = $Mg(OH)_2$
It reacts very slowly, has upper pH limitation, relatively safe to handle

Soda ash = sodium carbonate = Na_2CO_3
It reacts quickly, relatively safe to handle

At this point, the actual chemistry of neutralization is finished and the physics part begins. Do not despair, you do not need to be an Einstein to understand it; perhaps a Newton, but not an Einstein.

7.0. **The Physics In Waste Water Treatment**

The byproduct ferrous hydroxide is a very fine slimy sludge and green in color; it is insoluble and therefore suspended in the solution. It needs to be removed from the water. If the neutralized solution is aerated, the ferrous hydroxide may oxidize to brown ferric hydroxide, which is less slimy, but usually forms finer solid particles.

7.1. Settling

Settling means to give a particle in a solution a chance to fall through the solution by it's own weight or mass.

Observe a rock falling through turbulent water versus a grain of sand (miniature rock). Which falls faster and why?

The rock falls to the bottom and the grain of sand remains suspended because the rock is heavy enough to overcome the drag. By reducing the velocity of the water, the sand will also settle.

Therefore by stilling a moving stream of water enough for the weight of fine particles to overcome the velocity of the water, the particles will settle.

To reduce the velocity of a solution, one must change its direction and increase it's containment volume. **A stilling vessel is needed**.

7.2. Agglomeration

If the grain of sand had a chance to cling to another grain of sand and another and another etc.,, the weight of the combined grains eventually will overcome the drag and therefore have a chance to settle also.

In order to keep stilling vessels within reasonable size, agglomeration is necessary. A chemical (polymer) which causes particles to attract one another is introduced after neutralizing, to agglomerate the fine particles into larger flocs as they are called. This process is often referred to as **flocculation**.

7.3. Thickening

When the flocculated solids settle, they are very fluffy and would be difficult to separate from the water. However, if the settled material is allowed to stand for a period of time, the fluffy particles will compact into one another and create a **thickened sludge** which will be much easier to remove from the bottom of a vessel. Even so, this thickened sludge is still very thin; it contains only 1 to 2% solids

7.4. Separation/Dewatering

To separate the settled solids from the water, they must be passed through equipment which will allow water to pass but solids to stay behind.

This can be accomplished by filtration. Many types of filtration equipment are available; the type needed must be chosen carefully for each application. Most filtration equipment is designed to also take care of dewatering. This is the process used to make more solid cake out of the relatively soft and watery filtered material so that hauling costs stay at a minimum. The resultant filter cake will contain 30 to 45% solids when lime is used as a neutralizer, with others it will be 20 to 25%.

7.5. Gravity Flow

Because liquid flows in waste water treatment plants are relatively small and designed for low velocity, the process is usually laid out so that liquid streams can flow from vessel to vessel by 'gravity' meaning there is a fall or elevation difference between vessels. The ulterior motive is less pumping, less mechanical equipment and therefore also less costs.

7.6. Agitation

In order for the reactions to take place quickly and to assure good readouts on the control instruments, it is important to mix the chemicals with the waste water thoroughly. All neutralizers therefore are equipped with agitators or stirrers. These are designed to keep the solids in suspension until they reach the stilling vessel.

8.0. **The Process** (read with diagram 'fig.2')

The following is a generic description of a typical waste water treatment plant. In reality, most treatment plants are custom designed to suit the pickling process they are part of, and may contain more or less equipment than as shown in figure 2.

The collected waste water from rinsing, fume scrubbing and containment sumps is collected in a waste water holding tank or pit. From there it is pumped at a relatively steady rate to the neutralizer which is elevated high enough to provide gravity flow from there through the entire process.

The waste water enters at the top of the first stage of the neutralizer then underflows into the bottom of the second stage, then overflows to the bottom of the flocculation tank.

Each neutralization stage is equipped with a pH controller and a metering pump which adds the neutralizing chemical based on the acidity measured by the instrument. Both neutralizing vessels are equipped with stirrers. The chemical reactions that form the insoluble sludge particles take place in these two vessels.

Although metal hydroxides formed in the neutralizers are settling agents in their own right, the formation of floc is slow, which would make settling vessels too large. Therefore flocculating agents in the form of polymers are added to speed up the process.

The flocculating agent is added to the pipe line between the second stage neutralizer and the flocculating tank by a metering pump. In the flocculation tank, the solids must be given a chance to agglomerate but not settle; therefore agitation in this tank must be very gentle; in some cases the natural movement of the water is enough.

The treated waste water containing fast settling solids then overflows the flocculation tank and enters the center of the clarifier through a dip tube which is submerged in the pool of relatively still water. Because of the size of the vessel, the water flows very slowly from the dip tube to the circumference of the overflow weir.

As the water travels slowly across the radius of the vessel and up to the weir (change of direction and larger volume), the solids are given a chance to settle and accumulate in the bottom of the clarifier and the treated water, free of solids, overflows the weir into the sewer. The clarifier described here and shown in the diagram is a conventional type. There are other clarifiers available which take up less space but the principal is essentially the same.

The solids in the clarifier get compacted somewhat because of the prolonged residence time and are allowed to flow to a sludge storage tank. This tank is needed to provide time delay for filtration operations and/or maintenance problems on the filtration equipment. From this tank figure 2

the sludge is pumped via a positive displacement pump to the filtration equipment which in the diagram is shown as a filter press.

The sludge is held back in the cloth pockets between the filter plates and the water passes through the cloths and is put back into the clarifier, because no filtration equipment is good enough to remove 100% of the solids.

The sludge, after being dewatered in this case by using plant air, is removed by opening the filter press and dropping the sludge cake into a disposal container.

This concludes the description of the process; what we need to know now is how to control it.

9.0. Controlling The Process

9.1. Process Flow

After all of the necessary precautions have been implemented on the pickle line, to reduce the waste water flow to the treatment plant, there remains a relatively small flow to be taken care of. This **waste water needs to be put through the treatment plant at a steady flow** because the controls on this system work best when there are the least flow fluctuations.

This is best accomplished by having a fairly large collection vessel with a proportional level control operating a control valve on the waste water pump discharge. Another method would be to have a proportional level control operate a variable speed pump. As a result, fluctuations in flow entering the collection tank are distributed over a longer period of time before entering the 1st stage neutralizer.

9.2. Neutralizers

This is the most important section of the process to control and also the most difficult. In these two stages of neutralizing all of the dissolved solids must be changed to insoluble solids. This is done by changing the acidic waste water into basic waste water. The range of pH at which this is happening is so narrow that very sensitive instruments are required to measure it and interpret the measurements into chemical additions required.

9.2.1 Determination Of Acid Or Base By pH Method

9.2.1.1 *What is pH?*

When acidic or basic solutions are very weak, measurement of their concentrations by conventional methods (titration) becomes very difficult. Just saying "it's basic" or "it's acidic" does not tell us how basic or how acidic the solution is. This would be like saying the temperature is warm or cold, which does not really mean too much until one compares it to the temperature scale on a thermometer.

To give us a chance in defining how acidic or how basic a solution is, a scale to measure this was developed. The scale is based on the fact that hydrogen ions are freed or tied up, when acidic or basic materials are dissolved in water. To find out why and how this comes about you must consult a chemistry text book. For the purpose of this discussion, we simply accept the fact that the pH scale consists of 14 pH units from 0 to 14 with 7 being the neutral point (neither basic nor acidic)

The acidic side is represented by the pH units from 0 to 7
The basic side is represented by the pH units from 7 to 14

0 represents strong acid
7 represents neutral (pure water)
14 represents strong base (alkali)

The actual scale shown below has been developed using hydrogen chloride (hydrochloric acid, muriatic acid, HCl) and sodium hydroxide (caustic soda, NaOH) as a reference for the pH units:

3.6 % HCl = pH 0
4.0 % NaOH = pH 14

Every unit between these values and pH 7 represents a 1/10th dilution of the previous unit. i. e.

pH 0 = 3.6 % HCl
pH 1 = 0.36 % HCl
pH 2 = 0.036 % HCl
etc. etc.

A comparison of % acid or base versus pH units would therefore look like this:

	pH		%		
	0	=	3.6		
	1	=	0.36		
	2	=	0.036		
	3	=	0.0036		
	4	=	0.00036		
	5	=	0.000036		
Acid	6	=	0.0000036	HCl	
Pure Water- - - -	7- - - - -	=- - - -	- - - - - - 0.0000000- - - - - - - - -		- - - - -
Base	8	=	0.000004	NaOH	
	9	=	0.00004		
	10	=	0.0004		
	11	=	0.004		
	12	=	0.04		
	13	=	0.4		
	14	=	4.0		

As you can see, pH measurement of acidic or basic solutions can only be used up to a 3.6 % equivalent of HCl or a 4.0 % equivalent of NaOH. At stronger concentrations the pH simply remains at 0 or 14 respectively. In practice however, because of the effects of concentration, it is not recommended to use pH measurement below pH 1 or above pH 13.

For example:

Determination of the pH in a solution containing more than 0.36 % acid would simply indicate a pH between 0 and 1.
Determination of the pH in a solution containing more than 0.4 % caustic would simply indicate a pH between 13 and 14.

Please be aware, that the comparison between pH and concentration as shown above only holds true for HCl and NaOH but is the basis of the pH scale. Other acids and bases and solutions containing salts compare differently in terms of their relationships between concentrations and pH and are not necessarily uniform with the scale.

Examples:

Sulfuric Acid (H_2SO_4):

pH 0 = 4.9 %
pH 1 = 0.49 %
pH 2 = 0.049 %
etc. (remains uniform, as most acids do)

Sodium Carbonate (Na_2CO_3 - soda ash):

pH 11.6 = 10.0 %
11.4 = 2.5%
11.2 = 0.6%
11.0 = 0.15%
10.8 = 0.05%
10.6 = 0.02%
10.4 = 0.01%
10.3 = 0.006%
etc. (not uniform, behavior of salt solutions is similar)

9.2.1.2 *MEASURING pH*

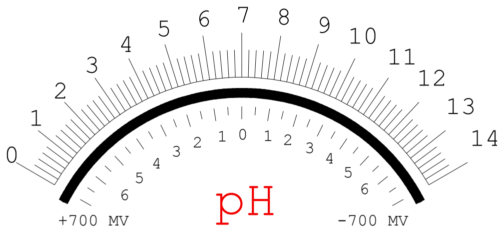
There are two methods available to us to measure pH:

- the pH meter
- pH paper (Litmus paper)

The **pH meter** is a very delicate instrument using electrodes immersed in the solution to be measured. For details of measurements by meter or instrument, please consult the instructions given by the manufacturer of the meter or instrument and electrodes being used!

The principle of measurement is based on electrochemistry, which means that a voltage is produced when two electrodes of dissimilar makeup are immersed in an electrolyte (This is how a battery works).

The pH probes when immersed in the solution to be measured create a millivoltage which is indicated on the meter scale. Converting the millivolts to pH units allows us to read the pH directly from the meter scale:



positive 0 to 700 mV = pH 7 to 0 (acidic)

negative 0 to 700 mV = pH 7 to 14(alkali)

Extreme care and vigilance is necessary in keeping the electrodes free of dirt and chemical deposits. Also careful standardisation of pH meters or instruments is necessary frequently, to assure accurate readings (consult manufacturer's operating instructions).

Using pH paper is the simplest and fastest but not necessarily the most accurate method of measuring pH. The paper used for this purpose is treated with chemicals which change colour according to the pH value of the solution it is immersed in. Together with the pH paper you purchase is a colour comparison chart. Without this chart the pH paper would be useless, as the colour of the wet paper must be compared with the chart to determine the pH value measured.

The colour range varies depending on the sensitivity (pH-range) the paper is made for. In general, you will find the following extremities:

Highly acidic	Red
Neutral	Yellow
Highly basic	Navy Blue

If the solution to be measured is coloured or dirty or sludgy, the paper colour relating to the pH measurement will be very difficult to read and washing the dirt off with water would tend to change the colour.

There are however pH papers available which are made to be washed after immersion. These are very accurate and highly recommended. Usually they are manufactured as small plastic strips with sensitive paper coating on one end and are sometimes referred to as "pH sticks".

A final warning about pH measurement: Regardless of what method is used, pH can only be measured in aqueous solutions! i.e. solutions containing water.

9.2.2. *Chemical Additions*

At approximately pH 4 to 5, the metal salts start converting to hydroxides; therefore the first stage of neutralizing should be maintained at pH 6. The second stage then refines the pH to what is allowable in the sewer stream. This varies between pH 8 to 10, depending on municipal regulations. It is also important to note, that if there is zinc present in the waste water, the final pH can not exceed 10 because the zinc will start to go back into solution at a higher pH.

The pH levels are maintained by addition of highly basic materials such as caustic. This material is added to the agitated neutralizers by means of metering pumps. These pumps are controlled directly by a signal from the pH measuring/control instruments. The instrument adjusts the speed or on/off of the metering pump to maintain the pH as close as possible to the manually set control point (setpoint) on the instrument.

There are various types of metering pumps used; some have stroke and speed adjustments on the pumps, some only speed adjustments. Regardless of which type is used, these local adjustments must be set manually to suit the process by trial and error. These adjustments control the amount of chemical being pumped at any given time or impulse and therefore affect the under or overshoot of chemicals. When the ideal adjustment is found, they need not be changed again.

Because of the logarithmic nature of the pH scale it takes 10 times less neutralizing chemical to change the pH from 2 to 3 as it does to change it from 1 to 2. Similarly, it takes 10 times less neutralizing chemical to change the pH from 3 to 4 as it does to change from 2 to 3. This makes it very difficult to control pH accurately without very complex control systems. Most neutralizing systems compromise by using 2 or 3 metering pumps of different sizes, and accepting some variation in final pH.

9.2.3. *pH Probes*

These probes are very delicate pieces of equipment and must be handled accordingly. Also by the nature of their construction and technology used, the probes are susceptible to coating and electric drifting. **It is therefore of utmost importance, that these probes are cleaned and standardized at least once per week.**

Standardizing is done by making the appropriate adjustments on the instrument to read the pH of a known buffer solution that the probe is immersed in. Use the instrument and probe manufacturers instructions for the proper procedure.

A quick check on proper pH readout on the instruments on a daily basis can be done by simply checking the pH of each neutralizing vessel with pH paper or pH sticks or taking a sample and checking it on an independent pH meter

9.3. Polymer Addition

Polymers are sold in very concentrated forms, as thick as molasses. They must be mixed with water at very low concentrations to be used in the process. They are usually added to the mixing tank by use of a measuring cup, to create a 0.3% solution by volume. This solution is metered into the flowing neutralized water at a rate which will give a concentration of approximately 10 ppm (parts per million) in the flocculation tank.

It is not possible to actually measure or analyze to see if there is enough polymer added. The only way to find out if the right dosage is being used is by settling tests. The proper way to do this is to do what is referred to as "jar tests". This is too complicated to use on a routine basis and not actually necessary. Therefore, a simple settling test will suffice: fill a 500 ml cylinder with waste water that is flowing to the clarifier and observe the settling speed and clarity of the water above the settled sludge.

Based on this and a comparison with tests done in the past, the manual adjustments on the metering pump can be made:

> Under dosing will cause particles to float out of the clarifier weir (remain suspended in the test)
>
> Over dosing is a waste of polymer and will cause the sludge and tank walls to become sticky and eventually clog filtration equipment.

The other method is to actually calculate the required dosage, if the flow of waste water is fairly steady, if not, then adjustments by trial and error and the occasional settling test are sufficient control of this material.

9.4. Settling

All of the controls on the system thus far contribute to proper settling. Therefore, there is very little that can be controlled on a clarifier except for the sludge buildup. As the sludge level increases, it is necessary to remove sludge from the bottom, to try and maintain an acceptable sludge phase level.

This can be done batch wise by opening the drain valve as the sludge level rises to the top sample point and lowering it to the middle sample point. Or by adjusting the drain valve to maintain a steady flow so that the sludge level remains between the two top sample points.

There are instruments available to measure the sludge level and the clarity of the water leaving the weir. However, they are very expensive and must be maintained daily. The cost involved may be justified on very large treatment facilities but are usually out of reach and not really necessary for the average pickling operation.

One must just remember, that:

> Too high a sludge level causes turbulence in the stilling section and therefore solids in the overflow weir

Too low a sludge level causes 'ratholing' in the sludge bed, thus allowing too much water and not enough sludge to flow to the sludge tank.

9.5. Filtration

Because the filtration system is quite different on each treatment plant, the control of it will depend on the type of equipment used and therefore should be done according to manufacturers instructions.

Let it be sufficient to say, that regardless of the type of equipment used, it is important to keep the sludge tank level as low as possible at all times, so as to have storage space available when something goes wrong with the filtration equipment. Whatever controls there are on this equipment, the aim should be to dry the sludge as much as the equipment can tolerate (see section 7.4.)

10.0. General Comments

10.1. Vessel design

On very large processes, often the vessels are made of concrete. The reason for this is not quite clear, as the cost of concrete vessels is quite high as opposed to steel and/or plastic vessels. Perhaps external corrosion is one of the factors considered; upkeep in terms of coatings and painting.

On most pickle lines, waste water treatment vessels are custom designed and made of steel and/or plastic, because in most cases the process needs to be fit into available space. Making the vessels of steel or plastic gives much more flexibility in terms of placing them to suit the space available. As far as external corrosion is concerned, today's availability of relatively inexpensive quality coatings presents no problem.

10.2. Sizing The Plant

The final size and capacity requirements for a waste water treatment plant depends on the actual volume of waste water to be treated. If you are in need of a new plant or want to modify an existing one, it is most important to first do the following:

10.2.1. Cut back on obvious water wastage on the pickle line.

10.2.2. Have an independent survey done of your entire pickling system.

10.2.3. Based on that survey, make improvements to conserve and/or recycle water .

10.2.4. Have the waste water treatment plant designed based on the volume of waste water generated after improvements.

After all the above is taken care of operators will need to be trained on the new systems and the improvements made so that they understand the importance of using just enough water, never lots!

10.3. Staffing A Waste Water Treatment Plant

The ultimate treatment plant operation would be to be able to push a button and walk away. -------- It could be done, but the instrumentation costs would far outweigh the capital cost of equipment and installation. Therefore, in order to keep capital costs within reason (remember, there is no real payback on these systems), waste water treatment plants are designed to be operated by competent staff.

It is fair to say that this does not need to be done full time, but someone needs to patrol the system on a regular basis and look for potential problems in the offing and be competent enough to take action to avert the problem. This is in addition to the regular maintenance and calibration of pH probes and (if you have them) sludge level indicators and turbidity meters (water clarity indicators)

A waste water treatment plant as described in section 8 and 9 initially will need a technically competent person full time for a few weeks, to determine dosages and sludge movements. Eventually, this will turn into routine operations, and the actual hands-on time of this person could be cut to a ½ hour check every 4 hours provided the waste water flow is steady (no stop and go) and there are maintenance personnel available on demand.

Depending on the type of filtration installed, a separate person may be required for 1 hour each day to take care of the labor involved in moving the sludge.

On larger, more complicated systems such as when two separate streams of waste water must be treated separately (toxic and nontoxic) or if there are other systems put under this jurisdiction such as a waste acid and raw acid storage and waste acid processors, operator vigilance becomes more frequent and depending on the complexity of the systems may demand full time attention.

One of the most devastating decisions made in staffing a newly built or modified plant is to expect routine operation immediately upon startup. Thus no full time person is assigned, until things become routine. The plant will constantly be off balance and decisions will be made based upon disasters that will never happen once the plant is on steady flow.

New and modified systems must be given a chance to steady out and at the same time the operator will learn what is important during the eventual routine operation.

11.0. **Other Processes**

The basic waste water treatment systems described herein are quite conventional and proven operable and quite reliable. However, technology has progressed into this field also and several other systems, using different technology are now available:

11.1. Reverse Osmosis (RO)

This is where normal osmosis is reversed, by applying pressure to the acid side of the membrane thus making the water molecules flow through the membrane and holding the salt and acid molecules back.

These systems can be applied to acidic or neutralized waste water. However, there is a problem when used on acidic waste of finding membranes that will stand up to the acids. And, when used on neutralized waste water there are problems with scaling on the membrane.

Check with reputable RO specialists as to whether this method can be applied to your system.

11.2. Evaporation

If you have a source of waste heat available, it could be quite economical to evaporate the water out of the waste water and returning the concentrated solution to the pickle tanks.

Again here, as with all other systems it is important to evaluate first what you have and what could be utilized, before deciding if this is feasible.

11.3. Ion Exchange

You are probably familiar with water softeners, be it for domestic use or to remove calcium from boiler feed water. Since we are also dealing with salts in waste water, the same technology could be applied also. However, the presence of acid can be a problem here also.

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OTHER WHYS AND HOWS

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Whys and Hows of Hydrochloric Acid Pickling

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