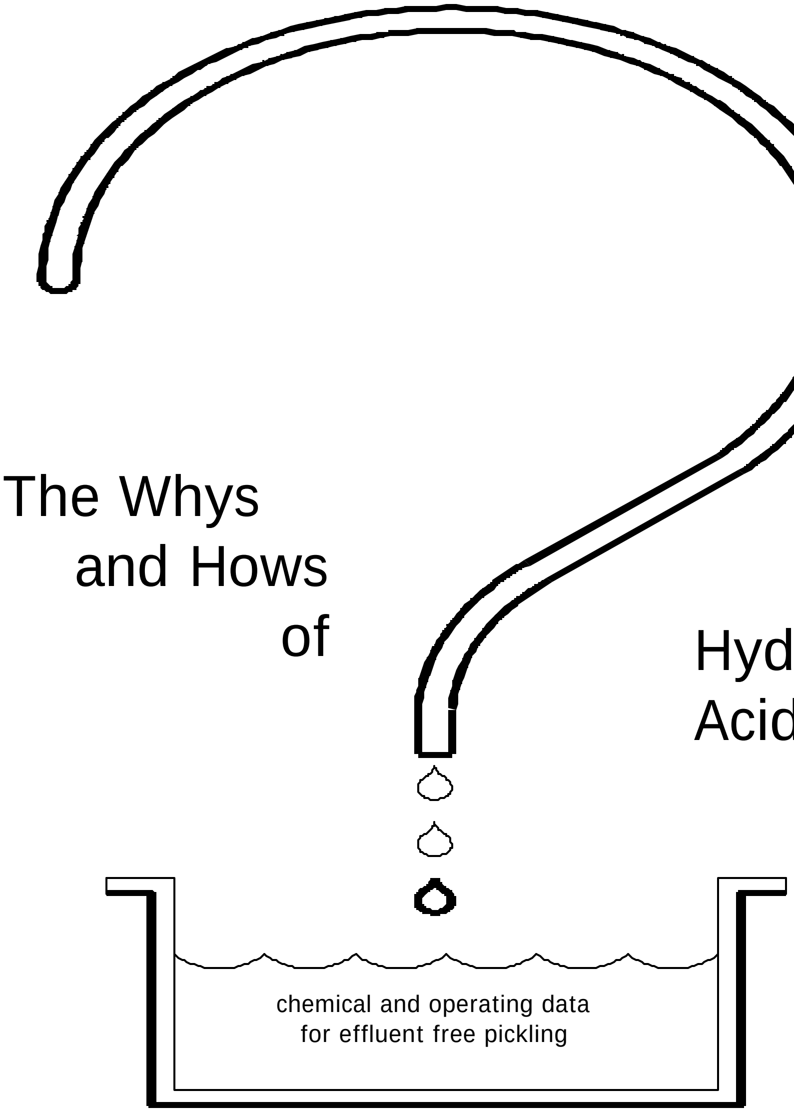
The Whys and Hows of Hydrochloric Acid Pickling



chemical and operating data
for effluent free pickling

Fred Hasler
Field Technician

Neil Stone
Chief Engineer

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Esco Engineering
179 Lansdowne Avenue,
Kingsville, Ontario N9Y 3J2
Phone: (519)-733-3122
Fax: (519) 733-6094

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1. **What Is Steel Pickling**

1.1 A Scaly Crust

When steel is cooling, after hot-rolling, the oxygen in the atmosphere chemically reacts with the hot surface iron on the steel and forms a compound normally referred to as SCALE.

Chemically speaking, this scale can be made up of one or any or all of these separate compounds:

Ferrous Oxide	-	scale (black, scaly)
Ferric Oxide	-	rust (brown, powdery)
Ferrous-Ferric Oxide	-	magnetite (blue black, magnetic)

This scale, no matter what proportion of the three above compounds it contains, is generally a very hard, brittle coating, from between paper thick to 1/32” thick, adhering to the surface of the steel.

No ‘foreign’ material can be present when the steel is further processed such as in sizing by cold rolling or drawing or forming by stamping etc. This means that the scale must be removed prior to this processing.

Mechanical scale removal methods such as:

shot blasting
brushing
grinding
scraping

damage the surface of the steel. In addition, the processes are usually self destructive and a constant maintenance headache.

As an alternative, chemical processing allows for quick, clean removal of scale, without mechanical damage to the steel surface and without using self-destructing equipment.

This method of scale removal is commonly referred to as

‘STEEL PICKLING’

Although it bears no relationship to ‘pickling’ in the general sense of the word, it does, however, imply the use of acid as the main process medium, which in turn leads us to chemical processing.

This means that the scale is being removed using chemical reactions with acids such as sulfuric or hydrochloric.

1.2 The History

1.2.1 *Lemon Juice and Vinegar*

Acid has been used to clean metals for centuries, both in the home and in industry. In the home, weak, safe acids such as vinegar and lemon juice are often used to clean cooking utensils of tarnish, and everyone knows that Coca-Cola is a good rust remover (it contains phosphoric acid). In industry, an early application of acid cleaning was the use of ‘killed spirits’ (hydrochloric acid with zinc added) as a cleaner and flux in soldering.

1.2.2 *The Iron Age*

As steel became available in the mid-nineteenth century, extensive metalworking industries grew up, requiring large amounts of clean, descaled metal. Most companies cleaned their own steel, and a metalworking shop would usually have a 'cleaning house', where the raw material was laboriously dipped in acid contained in a wood vat, then rinsed with copious amounts of water, and finally oiled or limed to prevent rusting of the clean surface; of course, waste solutions and rinsewater were simply poured into the nearest stream or river. To this day, many metalworking shops still call their pickling facilities 'cleaning houses'.

Most early picklers used sulfuric acid - it was cheap, readily available, easy to handle and did not make much fume or smell in use. As time passed, the wish to get more production and better quality led to various improvements in the process; mechanical handling on racks, heating the acid, use of inhibitors, use of acid-brick lined tanks. The system remained, however, essentially batch pickling in sulfuric acid.

1.2.3 *The Industrial Revolution*

The huge increase in demand for strip steel for automobiles and cans eventually led to the development of continuous strip picklers, in which the uncoiled strip was drawn continuously through tubs of hot sulfuric acid. Early lines processed several narrow strips at speeds of 30 to 100 fpm, with the successive coils being held together with mechanical clips, but, in time, speeds of up to 400 fpm were obtained with welding of each coil to the next - accumulators or looping pits were added to keep the pickler on stream while the welding was taking place.

1.2.4 *A New Acid On the Scene*

In the early 1960's a major change in high speed pickling technology took place - the introduction of hydrochloric (muriatic) acid pickling. Some specialty picklers had used hydrochloric acid previously, especially if a high quality surface was needed, but the expense, corrosiveness and fuming problems made this acid unattractive.
However, from 1960 to 1965, three things took place to change this:

- the development of light-weight, strong and cheap plastics materials, such as FRP and polypropylene, which made corrosion and fume control easier
- the development of processes to regenerate (or reclaim) the spent acid - not just the free acid, but also the acid that had reacted with the scale
- the increasing public awareness of the damage to the environment that results from dumping spent pickle acids into streams and rivers

Strip picklers then realised that hydrochloric acid could be an attractive alternative to sulfuric acid not only because it could be regenerated (so eliminating the pollution problem) but also because pickling speeds were higher, scale breakers were not needed, and product quality was better. As a result, by 1970 almost every major strip steel pickler in North America was converted to hydrochloric acid, and all new continuous lines use, without exception, hydrochloric acid.

1.3 The Acids

The difference in attack mechanism affects other aspects of pickling such as:

Surface finish:	Because the sulfuric acid has to attack the metal to remove scale, a sulfuric finish is usually more etched than a hydrochloric finish.
Inhibitors:	Because sulfuric has to attack the metal to remove scale, inhibitor cannot completely stop base metal attack. In hydrochloric acid, very effective inhibitors almost completely stop attack on base metal.
Scale breakers:	Hydrochloric acid dissolves scale, so no breakers are needed. In sulfuric acid the scale must be cracked to allow acid to penetrate beneath it.
Tank Sludge:	Sulfuric acid attacks scale very slowly, so removed scale collects in the bottom of the pickle tanks. Hydrochloric acid dissolves scale rapidly, so these accumulations do not occur. Also, at high temperatures, in sulfuric acid, ferrous sulphate monohydrate forms and settles out in the tanks, due to decreasing solubility at higher temperatures; this does not happen with hydrochloric acid.

Of course, hydrochloric acid has its disadvantages too:

- it is much more corrosive than sulfuric acid, which means pickle lines cost more
- it gives off choking fumes when hot, so very good fume exhaust systems are needed
- it is about 2 1/2 times as expensive as sulfuric acid

Because hydrochloric acid has so many advantages, the continuous high speed lines are now standard in the strip steel industry. These lines are characterized by:

- high speeds of 600 - 1200 fpm
- extensive hoods and fume exhaust systems
- complex acid systems

1.4 The Purse Strings

In former times, the main problem and expense in pickling was the handling of the steel, but in modern pickle lines, the situation is quite different. Nearly 85% of the cost of pickling is in the ‘wet system’ (acid/water system), the other 15% is in the handling of the steel.

With such a large expense for the acid system, it is obvious that a lot of effort is justified in making sure that it is working just right - after all a 10% saving in this area can be worth hundreds of thousands of dollars per year.

In the past, fuel and water were cheap, spent acid disposal was easy, and wastage was not very important, but in just the past few years many increased and extra costs have developed, for example:

	1977	1997	Increase
fuel per million BTU	$2.50 - 3.00	$3.00 - 3.50	up to 40%
city water per 1000 gal	$0.75	$1.00 - 2.00	1 1/2 - 2 times
sewage charges per 1000 gal	$0.50	$1.00 - 2.00	2 - 4 times
waste disposal costs per gal	$0.07 - 0.10	$0.50 - 1.00	7 - 10 times
acid - hydrochloric per ton	$50 - 60	$130	2 times

It is now no longer possible to live with the wasteful practices of the past - wasting acid, overheating tanks, throwing spent acid into the river. Nowadays, the chemical processing costs are the major cost in pickling steel, and this means that the pickle lines and acid reclamation system have to be looked upon and operated as **a complete chemical process**, instead of just a cleaning house and a recovery plant.

We have to learn how to get the most out of the modern equipment and materials.
What we did in the past no longer matters; it is what we can achieve in the future that counts.

2. <u>The Pickling System</u>

2.1 <u>Effluent Free - Now Possible</u>

It is impossible for a pickle line to be effluent-free?!?
This may appear to contradict what has already been said, yet it is true - it is not possible for a **pickle line** to be effluent-free, but it is possible for a **pickling system** to be effluent-free.

The reason why a pickle line alone cannot be free of effluent is very simple - what goes in must come out; we cannot destroy material, but only change it into a different form. This means that everything that is added to the pickle line must come out somewhere in some form. There are only three ways out:

- in the product
- down the drain
- up the stack

What goes into a pickle line?

steel
scale
dirt on steel
acid
water
inhibitor
steam
air

Only one of these is our desired product - clean steel; all the rest come out elsewhere, either as spent acid, rinsewater or exhaust air. Thus, in order to be effluent-free, it is necessary to have other equipment or processes to deal with the contaminated liquid or air, remove the contaminants and return them to the pickle line or convert them to other useful products. The combination of the pickle line and these various other units is **a pickling system, and it can be effluent-free.** But -- only by operating the pickle line and the other processes with consideration and understanding of the needs and limitations of the other parts of the process can the system work successfully. Just as a car only works if the engine and the transmission and the road gear and the electrics and the controls are all working properly, so in the pickle system, each part relies on the performance of the other to work properly.

2.2 Protecting The Environment

In the past the unwanted products from pickling - the contaminated water or dirty air - were simply dumped to the nearest river, or exhausted to atmosphere. At first environmental regulations required only concentrated spent acid to be cleaned up, but nowadays **plant discharges can virtually only be clear air and clean water**. In the past, the government rules have been backed up by persuasion and requests for co-operation, but recently local authorities have laid down some very serious money penalties for discharging untreated wastes. It is possible that one violation can increase the cost of pickling the steel by 50%! So there is a very strong reason for operating with little or no effluent leaving the system and if there is any at all, it must be clean.

2.3 The Quick Way Out (or how to chew up profits)

We have already said that a pickle system **can** be effluent-free, and many pickle systems are. However, no matter how well equipment is designed and maintained, anything can break down, and it is important to have some back up to cover this possibility.

This back up is provided by having installed spares where possible, and also by providing a waste facility - the chemical treatment system. If the acid system is not properly balanced, or if some recovery equipment is out of service, or not working efficiently, production is still possible by running wastes through the waste treatment system before discharge.

We must emphasize, however, that waste treatment is not the best answer to effluent treatment on a regular basis and it is not designed to handle the strong wastes. The acidic effluent and spent acid are treated with neutralizer to reduce acidity and unacceptable dissolved iron; these products become insoluble solids, which have to be removed as sludge and dumped elsewhere. Thus, it is a costly process involving expenses for:

- neutralizing chemicals
- chemicals to help solids settle
- sludge disposal
- operating and maintenance cost

all of which brings up the cost of products, without producing any useful materials.

This means, to help keep your costs, down, you should use waste treatment as little as possible, and then only for emergencies.

2.4 An Example Of What Can Be Done

As we explained above, in any system, what goes in must come out, somewhere.
To illustrate this, let us look at the changes made to a pickling system which was recently improved, to make it operate more economically and without waste.

In figure 1A we see the pickler alone, as it was before acid reclamation was installed.

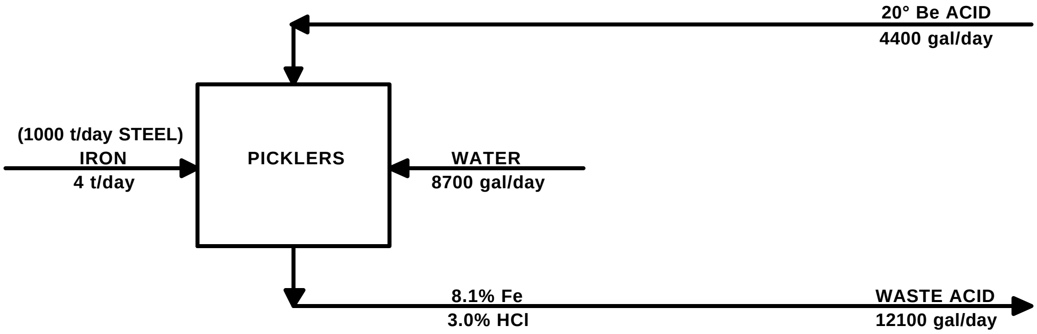


FIGURE 1A

4400 gal/day of raw acid, and 8700 gal/day of water were added to the pickler, and 12100 gal/day of hot, acidic, strong wastes were produced.

After acid reclamation was installed, the two systems were operated individually without consideration to balance the two between one another. What resulted was the situation illustrated in figure 1B.

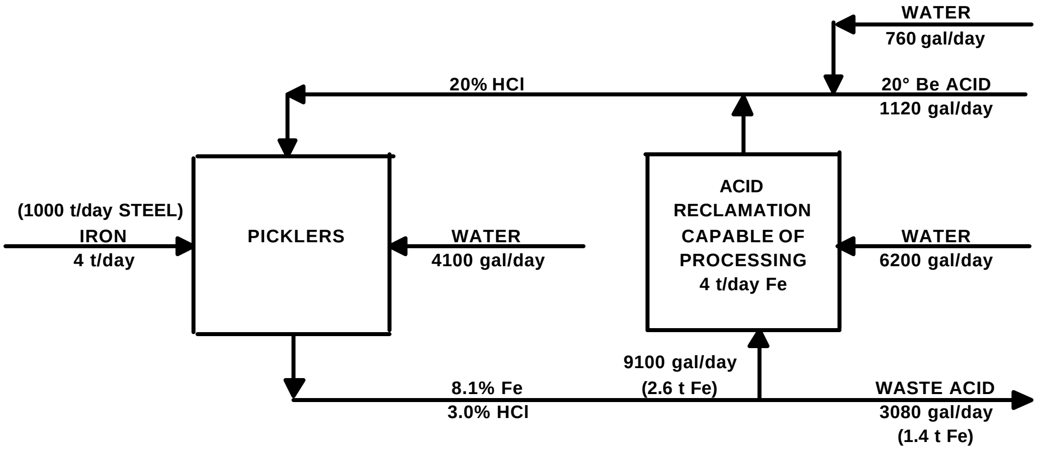


FIGURE 1B

12180 gal goes in, so 12180 gal must come out. Of this, 9100 gal goes to the reclamation plant (to produce 6200 gal of reclaimed acid) and the other 3080 gal must go as effluent.

After extensive reorganizing of the operating parameters and training of the operators in both processes to learn to operate the two as one acid system, considerable economical improvements were realized, the result of which is illustrated in figure 1C.

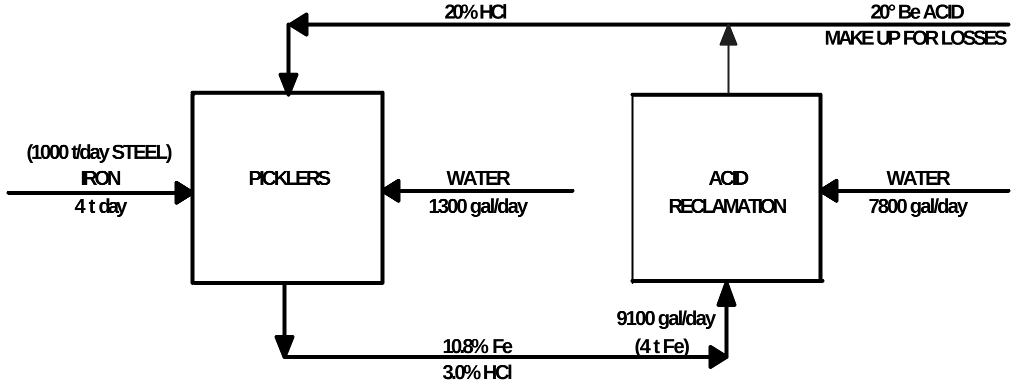


FIGURE 1C

By controlling the amount of water added to the pickle line and increasing the iron content of the spent acid, the discharge from the pickle line was reduced to 9100 gal/day, which all went to the reclamation plant - **No waste!**

The above examples illustrate how two individual processes can be integrated into one system by simply making the whole process balance, and by incorporating some basic principles of the laws of nature.

The above discussion was focused on balancing the acid stream in the system. But acid is not the only stream that can cause concerns, both environmentally and economically. The water usage in the system, if unbalanced and uncontrolled, can be one of the greatest causes of distress. Rinsing and fume scrubbing are the water consumers in the system and therefore also the waste water producers.

However, by incorporation of state of the art technology and proper process control, it is possible to make a pickling system totally effluent free. New or modified equipment may be needed to accomplish this, but the equipment and its operating procedures are only as good as the operator that works with them.

If your pickling system does not incorporate a recovery plant, then the waste acid is hauled away in which case the cost of hauling will offset the cost of operating a recovery plant. The same principles hold true: if you don't operate your acid system properly, your cost of disposal (or recovery) goes up. In order to run the **system** most efficiently, it is necessary to look at some of the reasons how and why things are done. For example:

- how much acid is really needed for pickling?
- how can some scrubbers work with so little water?
- why do we not need a lot of water for rinsing?
- why does weak spent acid cause problems in acid regeneration?
- how does each job affect other operations in the system?

To answer these and many other questions, we need to have some understanding of the basic theories behind it all.

3. **The Chemistry of Pickling**

3.1 Basic Chemistry We Should Know About

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

3.1.1 *A chemical reaction* is a happening where two physically and chemically different materials combine to form one or more materials physically and chemically different from the originals.

For example:

wood and air burn to form carbon dioxide and water
or in chemical terms
forms
hydro carbon + oxygen →→ carbon dioxide and water

3.1.2 *A physical change* (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

3.1.3 *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).

3.1.4 *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

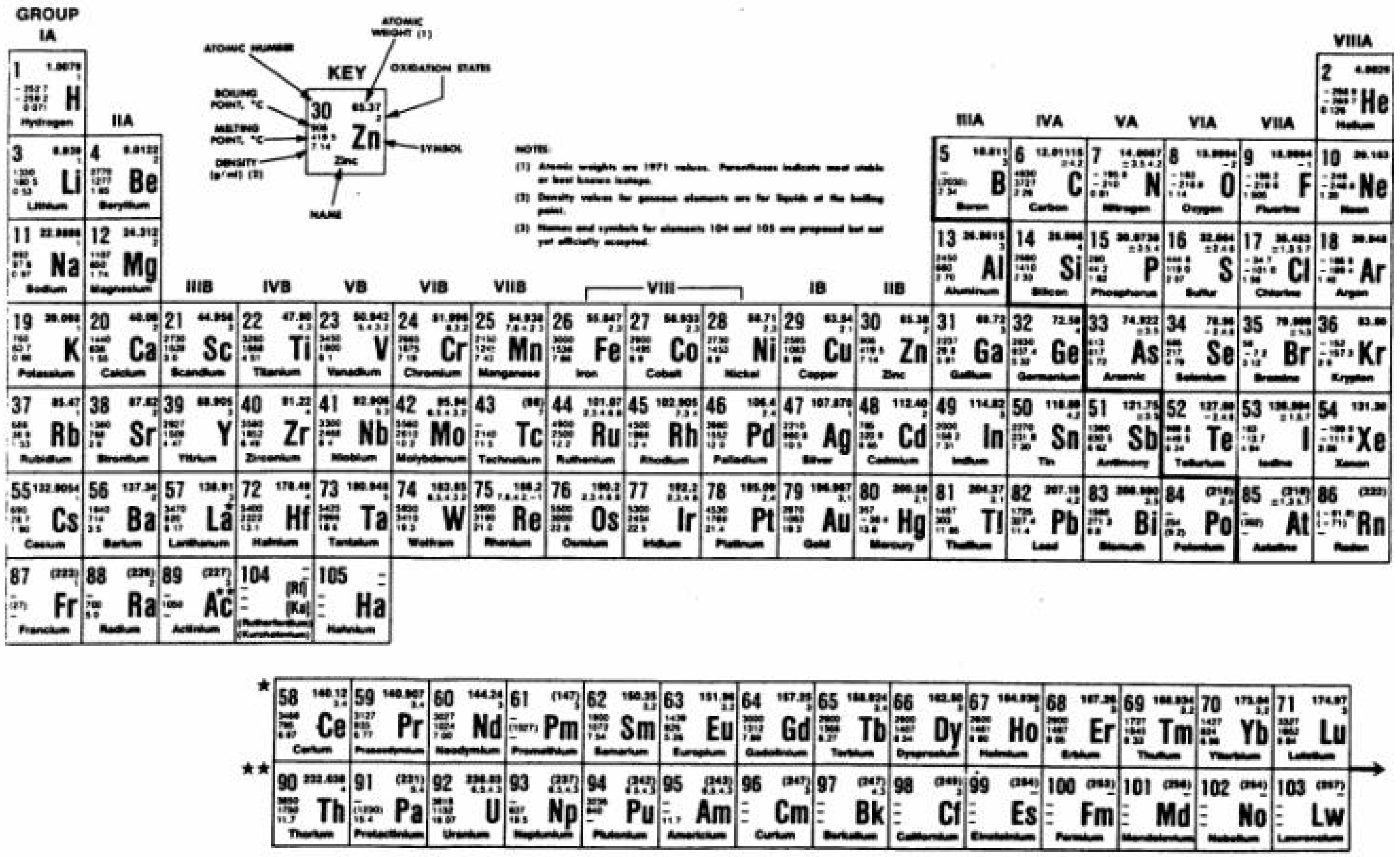
3.1.5 *All atoms have atomic specific weights* based on hydrogen being 1. When combined into molecules, the sum of the weights of the atoms in the molecule is called the molecular weight.

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.

PERIODIC TABLE OF THE ELEMENTS



NOTES:

(1) Atomic weights are 1971 values. Parentheses indicate most stable or best known isotope.

(2) Density values for gaseous elements are for liquids at the boiling point.

(3) Names and symbols for elements 104 and 105 are proposed but not yet officially accepted.

GROUP IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La* Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Wolfram	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac** Actinium	104 [Rf] [Ku] (Rutherfordium) (Kurchatovium)	105 Ha Hahnium													

*	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
**	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lw Lawrencium

FIGURE 2

Atomic weights are listed in the periodic table of elements (figure 2). 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

3.1.6 *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 one 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 pickling are:

hydrogen chloride	= HCl	(one H	+	one Cl)
scale (iron oxide)	= FeO	(one Fe	+	one O)
rust	= Fe_2O_3	(two Fe	+	three O)
magnetite	= Fe_3O_4	(three Fe	+	four O)
ferrous chloride	= $FeCl_2$	(one Fe	+	two Cl)
ferric chloride	= $FeCl_3$	(one Fe	+	three Cl)
water	= H_2O	(two H	+	one O)
hydrogen	= H_2	(one H	+	one H)

3.1.7 *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:

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

From the discussion in 3.1.6 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.

3.1.8 *Molecular Weights Are Also In Balance*

For example:

the unbalanced equation as in 3.1.7 above would be expressed in atomic weights thus:

$$\begin{array}{lcl} \mathrm{FeO} + \mathrm{HCl} & \rightarrow\rightarrow & \mathrm{FeCl_2} + \mathrm{H_2O} \\ (56 + 16) + (1 + 35.5) & = & (56 + 71) + (2 + 16) \\ \text{total } 108.5 & \text{(not equal)} & \text{total } 145 \end{array}$$

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

$$\begin{array}{lcl} \mathrm{FeO} + 2\mathrm{HCl} & \rightarrow\rightarrow & \mathrm{FeCl_2} + \mathrm{H_2O} \\ (56 + 16) + 2x(1 + 35.5) & = & (56 + 71) + (2 + 16) \\ \text{total } 145 & \text{(balanced)} & \text{total } 145 \end{array}$$

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

$$\begin{array}{lcl} \mathrm{FeO} + 2\ \mathrm{HCl} & \rightarrow\rightarrow & \mathrm{FeCl_2} + \mathrm{H_2O} \\ 72 + 73 & = & 127 + 18 \end{array}$$

3.1.9 Since *atomic weights are an indication of the weight ratio* by which molecules will react with one another, it follows that by substituting the atomic 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 3.1.8 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.

3.1.10 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 3.1.9 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.

3.2 Chemical Reactions In Pickling

When steel is immersed in hydrochloric acid in a pickle tank, two reactions take place.

3.2.1 *Scale is dissolved*:

$$\begin{array}{ccccccc} FeO & + & 2HCl & = & FeCl_2 & + & H_2O \\ \text{scale} & + & \text{acid} & = & \text{ferrous chloride} & + & \text{water} \\ 72 & + & 73 & = & 127 & + & 18 \\ & 145 & & = & & 145 & \end{array}$$

If there is rust or magnetite on the steel, these will produce ferric chloride ($FeCl_3$), thus:

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$

$$Fe_3O_4 + 8\,HCl \rightarrow\rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$$

3.2.2 *Base metal is dissolved*:

$$\begin{array}{ccccccc} Fe & + & 2HCl & = & FeCl_2 & + & H_2\ \text{(gas)} \\ \text{steel} & + & \text{acid} & = & \text{ferrous chloride} & + & \text{hydrogen} \\ 56 & + & 73 & = & 127 & + & 2 \\ & 129 & & = & & 129 & \end{array}$$

We want the first reaction (3.2.1) to take place, because this is what removes the scale. We don't want the second reaction to take place because it uses up acid and etches the steel; this is why we use inhibitor.

Base metal is also dissolved by reaction with ferric chloride (produced by rust or magnetite) (see 3.2.1).

$$2FeCl_3 + Fe \rightarrow\rightarrow 3FeCl_2$$

This cannot be inhibited and is the reason why pickle acid never contains ferric chloride.

3.2.3 *Both these reactions take place in solvent water*. In the acid reclamation plant, we can make the reactions go the other way by taking away the solvent.

The spent acid is added to a very hot reactor, so that the water evaporates to produce steam (a physical change). Then, the solid ferrous chloride reacts with the steam under the influence of heat to change the ferrous chloride back to iron oxide and acid:

$$FeCl_2 + H_2O \overset{\text{add heat}}{\rightarrow\rightarrow} FeO + 2HCl \text{ (gas)}$$

ferrous chloride + water = iron oxide + hydrogen chloride
127 + 18 = 72 + 73
145 = 145

3.2.4 *Because of the hot air in the reactor,* the iron oxide is actually produced in a different form,

$2FeO$	+	O	=	Fe_2O_3
ferrous oxide	+	oxygen (in air)	=	ferric oxide
144	+	16	=	160
		160	=	160

However, as you can see, the reclamation reactor is only making the pickling reaction go backwards. Reclamation works because, in the hot reactor, there is no water to dissolve the hydrogen chloride gas produced in the reaction. Thus, the hydrogen chloride gas leaves from the reactor with the exhaust gases, and is collected by dissolving it in water, so it can be returned to the pickle line.

The chemistry of the whole system is illustrated in figure 3. There it can be seen that iron oxide as scale goes in, iron oxide as oxide pellets comes out and everything else goes around and around.

3.3 Hydrogen Chloride, A Gas

In order to use hydrochloric acid efficiently in pickling systems, we must understand a few of its characteristics.

3.3.1 *It Is Absorbed*

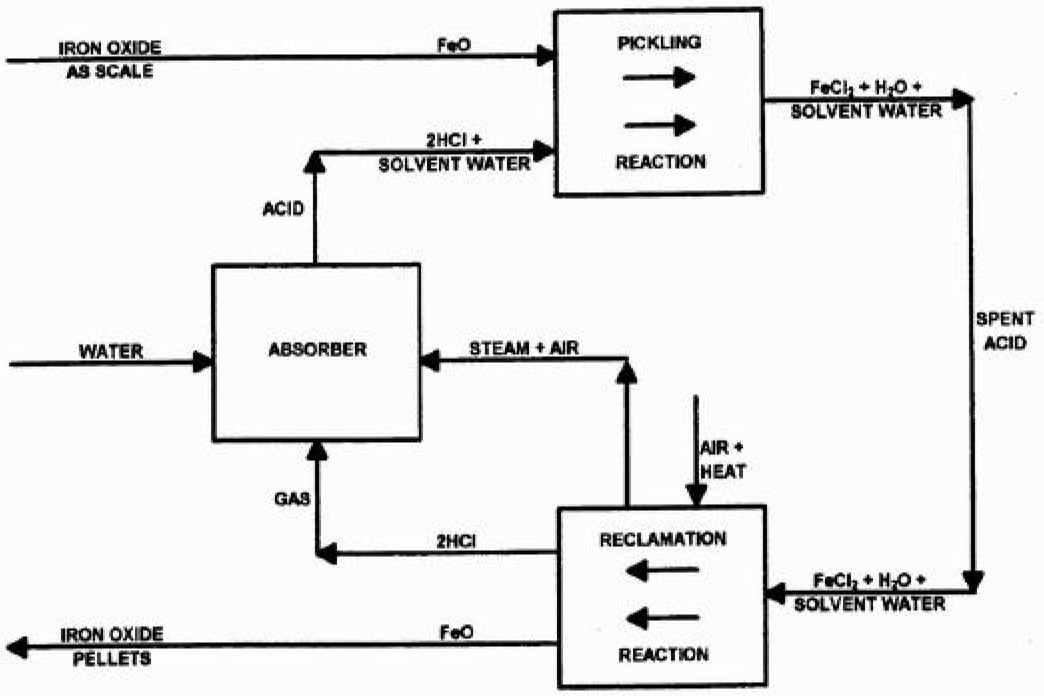
The acid is made by absorbing hydrogen chloride gas in water. The gas will dissolve in water only to a maximum concentration of 36% by weight due to equipment and transportation limitations. Most plants use 32% by weight (also called 20° Bé) acid which is less fuming.

3.3.2 *It Creates Vapor*

By far the most important characteristic is the vapor pressure. The vapor pressure of a solution is the pressure exerted by the vapor of the solution due to evaporation above the free liquid surface. It shows up as fumes coming off the acid.

FIGURE 3

THE CHEMISTRY OF THE PICKLING SYSTEM



SCALE GOES IN,
OXIDE COMES OUT,
AND EVERYTHING ELSE
GOES
ROUND AND ROUND

The vapor pressure charts (figures 4 and 5) indicate vapor pressures of HCl and water over pure HCl solutions at various temperatures. Using the chart, we can deduce the following:

1. 36% HCl boils under atmospheric pressure below 140°F.
2. 29.5% HCl boils under atmospheric pressure at 212°F.
3. HCl will evaporate at specific rates under specific conditions without boiling.

Point #3 above is the most important as far as the use of hydrochloric acid for pickling is concerned. These vapor pressures can be converted to concentrations using the fact that one standard atmosphere is 760 mm Hg pressure.

For instance, at a constant acid temperature of 176°F (80°C):

Acid Concentration	Vol % HCl in Vapor	Vol % water in Vapor
14%	$\frac{2.5 \times 100}{760} = 0.33\%$	$\frac{280 \times 100}{760} = 37\%$
12%	$\frac{1.4 \times 100}{760} = 0.18\%$	$\frac{290 \times 100}{760} = 38\%$
10%	$\frac{0.6 \times 100}{760} = 0.08\%$	$\frac{310 \times 100}{760} = 41\%$

(NOTE: the remainder of material in the vapor is air).

This demonstrates that just by changing the acid concentration from 14 to 10% the amount of HCl loss due to evaporation is reduced about four times, but the water evaporation remains almost constant.

The same calculation can be made for a change in temperature. For instance, at a constant acid concentration of 12%:

Temperature	Vol % HCl in Vapor	Vol % water in Vapor
158°F	0.68 mm = 0.09%	195 mm = 26%
167°F	0.95 mm = 0.13%	240 mm = 32%
176°F	1.4 mm = 0.18%	290 mm = 38%
185°F	1.9 mm = 0.25%	360 mm = 47%

This demonstrates that the HCl loss at 185°F is nearly 3 times as much as at 158°F and that a 9° temperature rise leads to two times as much increase in loss at 176° as it does at 158°. Note also the substantial increase in water vapor generated at the higher temperatures.

3.3.3 *Effect of Ferrous Chloride*

Another characteristic to consider is that when ferrous chloride is mixed with hydrochloric acid, the effect on the vapor pressure is as if the acid concentration was increased. Figures 6 and 7 give the vapor of HCl over pickling acids for various iron contents at typical pickling temperatures of 180°F and 140°F.

FIGURE 4

VAPOR PRESSURE OF HCL OVER WATER SOLUTIONS
(from Perry's Chemical Engineers' Handbook, 7th Ed, table 2-10)

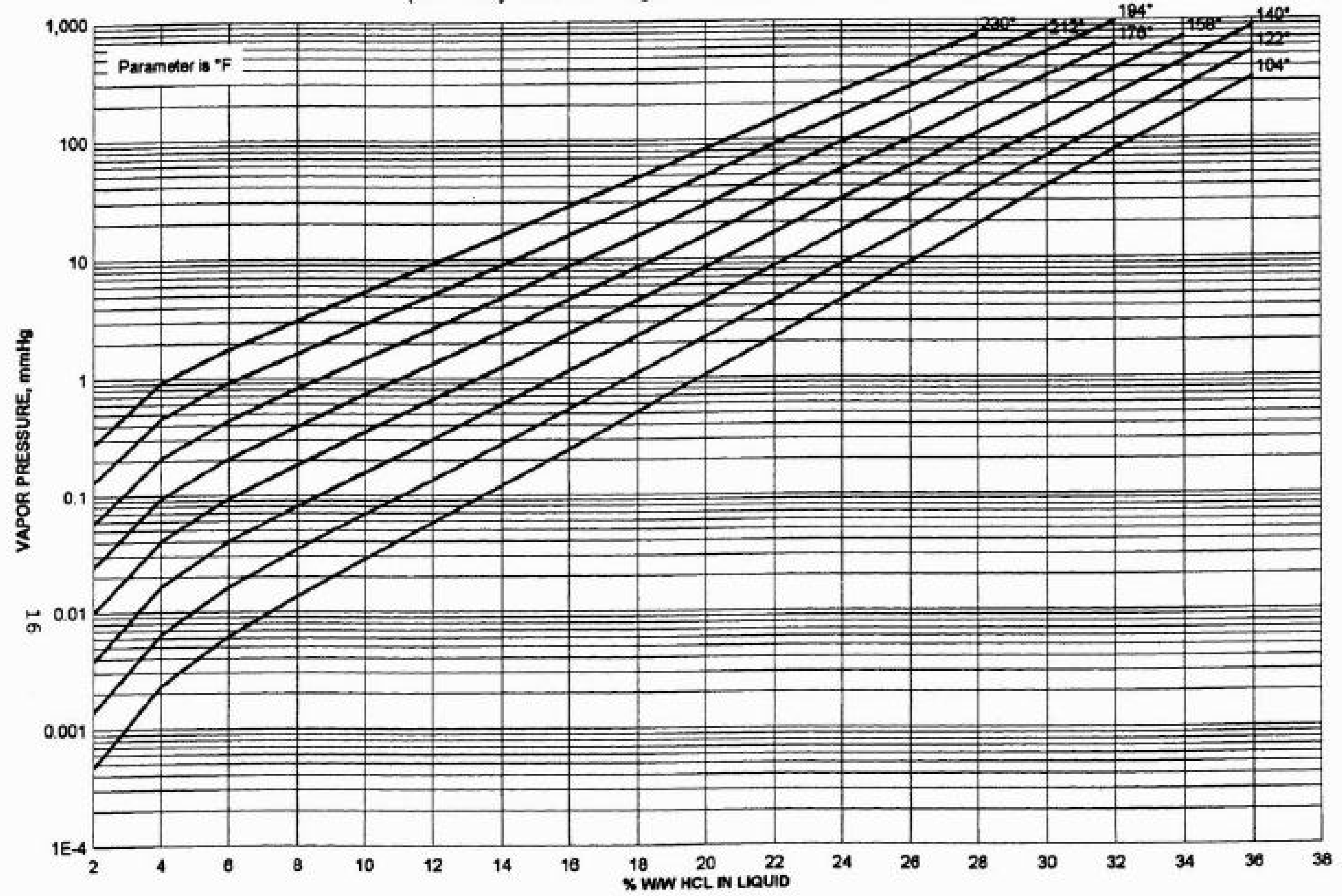
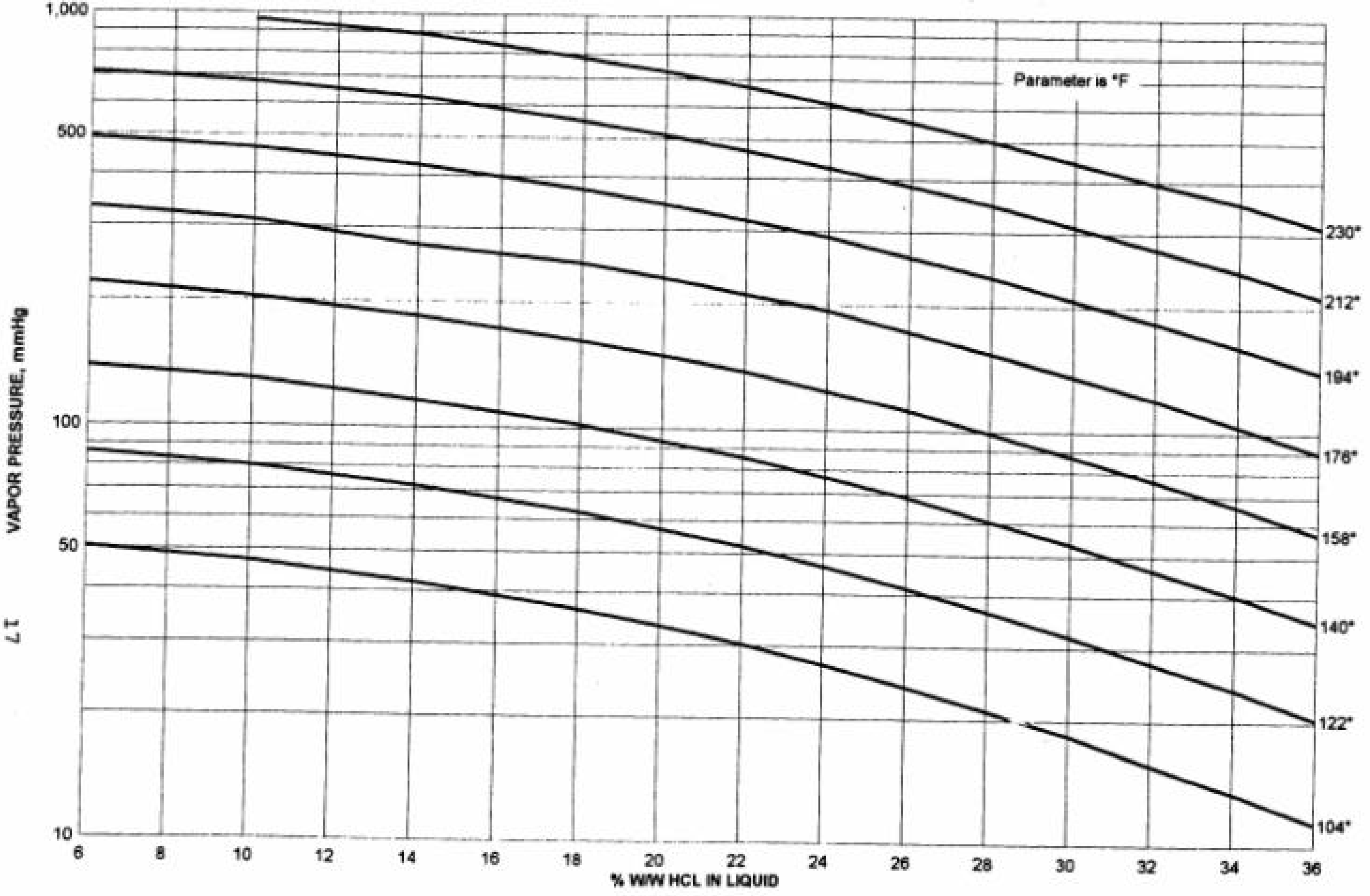


FIGURE 5

VAPOR PRESSURE OF WATER OVER HCL SOLUTIONS
(from Perry's Chemical Engineers' Handbook, 7th Ed, table 2-9)



Comparing, for example, a pickle acid containing 10% HCl and 6% iron at 140°F with a straight 10% acid solution, the vapor pressures are:

10% solution	10% pickle acid with 6% iron
0.16 mm Hg	0.9 mm Hg

or an increase of over five times.

3.3.4 *Hard On The Nose*

The acid and its vapors are very corrosive, thus making the solution quite hazardous to use. Increasing the temperature also increases this corrosivity, or, in other words, it speeds up the reactions. This, of course, is advantageous to dissolving scale, but is a disadvantage due to increased vapor losses.

This poses an increased threat to workers and equipment, warranting implementation of specific precautions.

OSHA regulations state that the maximum allowable concentration in a working area is not to exceed 5 ppm (parts per million) which is 5 cu.ft. HCl gas per million cu.ft. of air.

This accounts for the necessity for elaborate fume extraction systems. In areas where this limit is exceeded, appropriate respiratory protection must be worn.

Should acid spill on any part of the body at any strength, it must be washed off and diluted immediately by flushing with lots of water, for at least 15 minutes. DO NOT attempt to neutralize the acid on the affected area; it could cause severe complications in future treatment of the acid burn.

Knowing some facts about HCl, we can now attempt to make use of it for the purpose of steel pickling.

4. **Steel Pickling With Hydrochloric Acid**

4.1 What Happens

By submerging steel in acid, two main reactions take place. Both use hydrogen chloride and both produce ferrous chloride.

$$Fe + 2HCl \rightarrow\rightarrow FeCl_2 + H_2$$
$$FeO + 2HCl \rightarrow\rightarrow FeCl_2 + H_2O$$

The first reaction is where the acid reacts with the base metal (the steel under the scale). This reaction is quite slow and produces hydrogen gas as a byproduct, which accounts for the bubbling and foaming in the tank.

The second reaction is where the acid reacts with the scale itself. This reaction is much faster than the first and it produces water as a byproduct.

FIGURE 6

VAPOR PRESSURE OF HCL OVER PICKLE ACID AT 180°F
(from Akerkar & Shahani, NML Tech Journal, Vol 12, (1970), #11, 87-92)

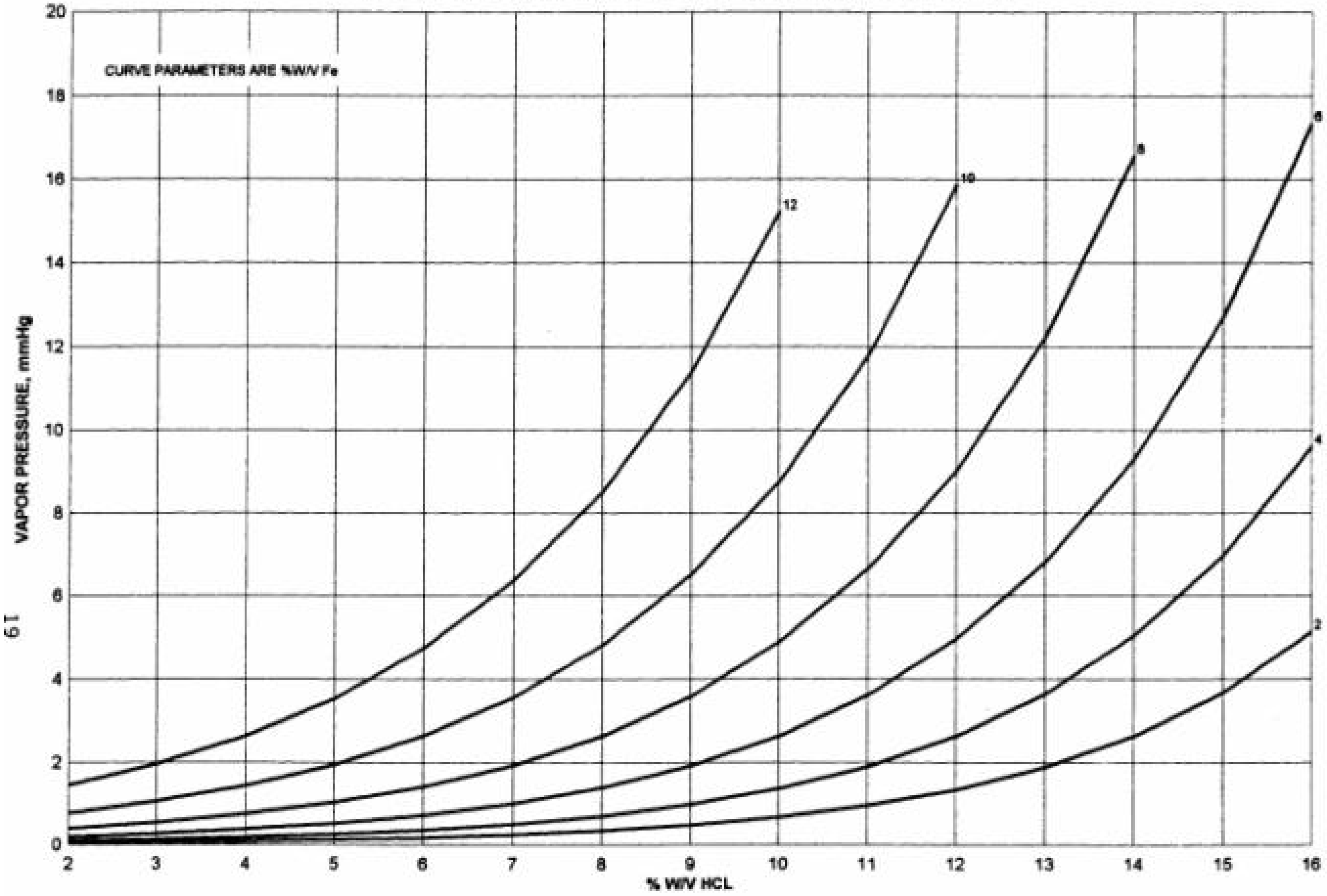
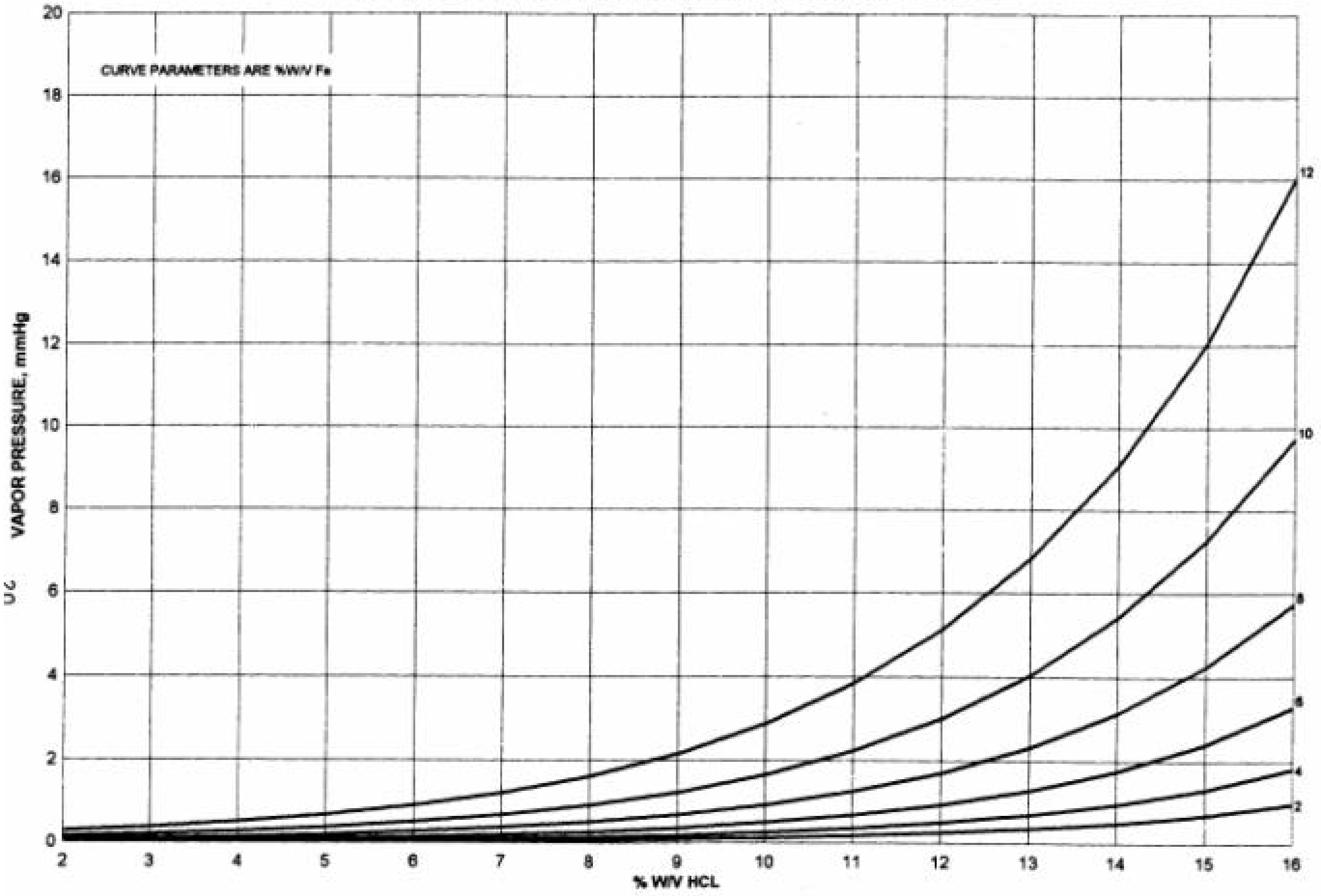


FIGURE 7

VAPOR PRESSURE OF HCL OVER PICKLE ACID AT 140°F
(from Akerkar & Shahani, NML Tech Journal, Vol 12, (1970), #11, 87-92)



It is in our interest to discourage the first reaction from taking place, since we are only interested in removing the scale. This is done by leaving the steel in the acid only as long as is absolutely necessary to remove the scale and by adding a chemical to the acid, which inhibits this reaction to the minimum (inhibitors are discussed later).

We can, therefore, stipulate that for all practical purposes the first reaction can be ignored.

4.2 How Much Acid Do We Need

By applying the chemistry we discussed above, we can now calculate the acid requirement to pickle one ton of steel, assuming an average iron loss of 0.35% (typical for pickling strip steel)

$$\begin{array}{lcl} FeO \quad + \; 2HCl & \rightarrow\rightarrow & FeCl_2 \; + \; H_2O \\ 56 + 16 + \quad 73 & & 127 \; + \; 18 \end{array}$$

73 lbs of hydrogen chloride (not acid) are required to react with 56 lbs of iron in the scale. Since one ton of steel has 0.35% of iron to be removed as scale, which is

$$\frac{2000 \text{ x } 0.35}{100} = 7 \text{ lbs, it follows}$$

that if 56 lbs Fe require 73 lbs HCl

then 7 lbs Fe requires $\frac{73 \text{ x } 7}{56}$ = approximately 9.13 lbs HCl (pure)

The acid we buy is shipped at 32 lbs HCl (gas) per 100 lbs of aqueous (in water) solution (32% concentration or 20° Bé), it follows then that

if 32 lbs HCl are dissolved in 100 lbs of solution

then 9 lbs HCl are dissolved in $\frac{100 \text{ x } 9.13}{32}$ = 28.5 lbs of solution

one gallon of 32% HCl acid weighs approximately 9.7 lbs; therefore, we will need __

$$\frac{28.5}{9.7} = 2.94 \text{ gals of 32\% acid}$$

This constitutes the theoretical or 'stoichiometric' amount of acid needed to pickle one ton of steel. Stoichiometric means as per chemical formula, using absolutely pure materials with no losses. In practice it is not possible to use up all the acid in the pickle tank if pickling is to be complete in any acceptable time. Depending on the pickling equipment, between 70% and 80% of the free acid will be used up in dissolving the scale, and 20 - 30% will remain as 'free' acid in the spent pickle liquor.

So finally we now know that between 3.6 and 4.2 gallons of 32% acid are needed to pickle 1 ton of steel (assuming the iron loss is 0.35%).

4.3 How Much Ferrous Chloride Do We Get

The amount of byproduct produced during the pickling of one ton of steel can also be determined in the same manner.

Since molecular weight 56 is equal to 7 lbs in the formula ratio, then molecular weight 127 is equal to:

$\frac{7 \times 127}{56}$ = 15.88 lbs $FeCl_2$ are produced per 1 ton of steel pickled

and molecular weight 18 is equal to

$\frac{7 \times 18}{56}$ = 2.25 lbs H_2O are produced per 1 ton of steel pickled

5.0 **Let's Get Practical**

It would be quite difficult, to say the least, to pickle 1 ton of steel in about 4 gallons of solution. To make it practical, we must not only have a larger volume of acid to put this steel into but we also need to heat it. Heating the solution increases the reaction rate thus dissolving scale faster, and therefore, increasing the pickling speed.

5.1 What To Do It In

Increasing the volume by dilution with water also makes the acid more acceptable to live with, i.e. less vapor. So, we have on one hand an advantage due to dilution and on the other hand, a disadvantage due to high temperature in terms of fuming or, more important, HCl loss due to evaporation. A compromise between four basic considerations is necessary.

- we want maximum temperature
- but we don't want to pay a fortune for heat
- we want maximum acid strength
- but we don't want to lose it through evaporation

Before we make this compromise, we need to know that the heat required to maintain the temperature of any given solution is dependent on:

- heat loss through the vessel
- heat loss due to cold steel being introduced
- heat loss due to evaporation

The last is the largest user of heat. As a rule of thumb, it can be said that heat requirement increases exponentially relative to temperature increases. For example, it takes one quarter more heat to maintain 160° as it does to maintain 150° and one quarter more to maintain 170° as it does to maintain 160° and so on.

To make the compromise we can see from the vapor pressure chart that the ideal conditions are between 10 and 14% HCl at 167° to 185°F (75 & 85°C) for continuous pickling in closed tanks. For batch pickling in open tanks, a lower temperature of 140°F (60°C) is used - higher temperatures lead to uncontrollable fuming.

5.2 Pickling A Batch Of Steel

Assuming now that the space required to pickle one ton of steel is a volume of 1000 gals and that we want to pickle at 10% acid, we can determine the amounts of water and acid to mix as follows:

5.2.1 *What Do We Need*

10% acid means 10 lbs of HCl (gas) per 100 lbs of solution. From the specific gravity curve (figure 8) we see that a 10% HCl solution has a specific gravity of 1.05,

hence one gallon will weigh 1.05 x 8.33 = 8.75 lb.

1000 gallons solution at 8.75 lb/gal = 8750 lbs.

A 10% solution will contain $\frac{8750 \times 10}{100}$ = 875 lbs HCl

875 lbs HCl at 32 lbs/100 lbs contain $\frac{875 \times 100}{32}$ = 2734 lbs of 32% acid

2734 lbs acid at 9.7 lbs/gal = $\frac{2734}{9.7}$ = 282 gals of 32% acid

We, therefore need

1000 - 282 = 718 gals water
\+ 282 gals 32% acid
= 1000 gals 10% acid

= 875 lbs HCl (gas) in 1000 gallons solution

5.2.2 *How Big A Batch Can We Pickle?*

As one ton of steel is being pickled in this solution, 9 lbs of HCl are used to combine with scale; this means that theoretically we could pickle

$\frac{875}{9.13}$ = 96 tons of steel

in this tank, without adding anything, assuming there is no evaporation.

Supposing we could pickle 96 tons of steel in this tank, without adding anything or removing anything, what would be left?

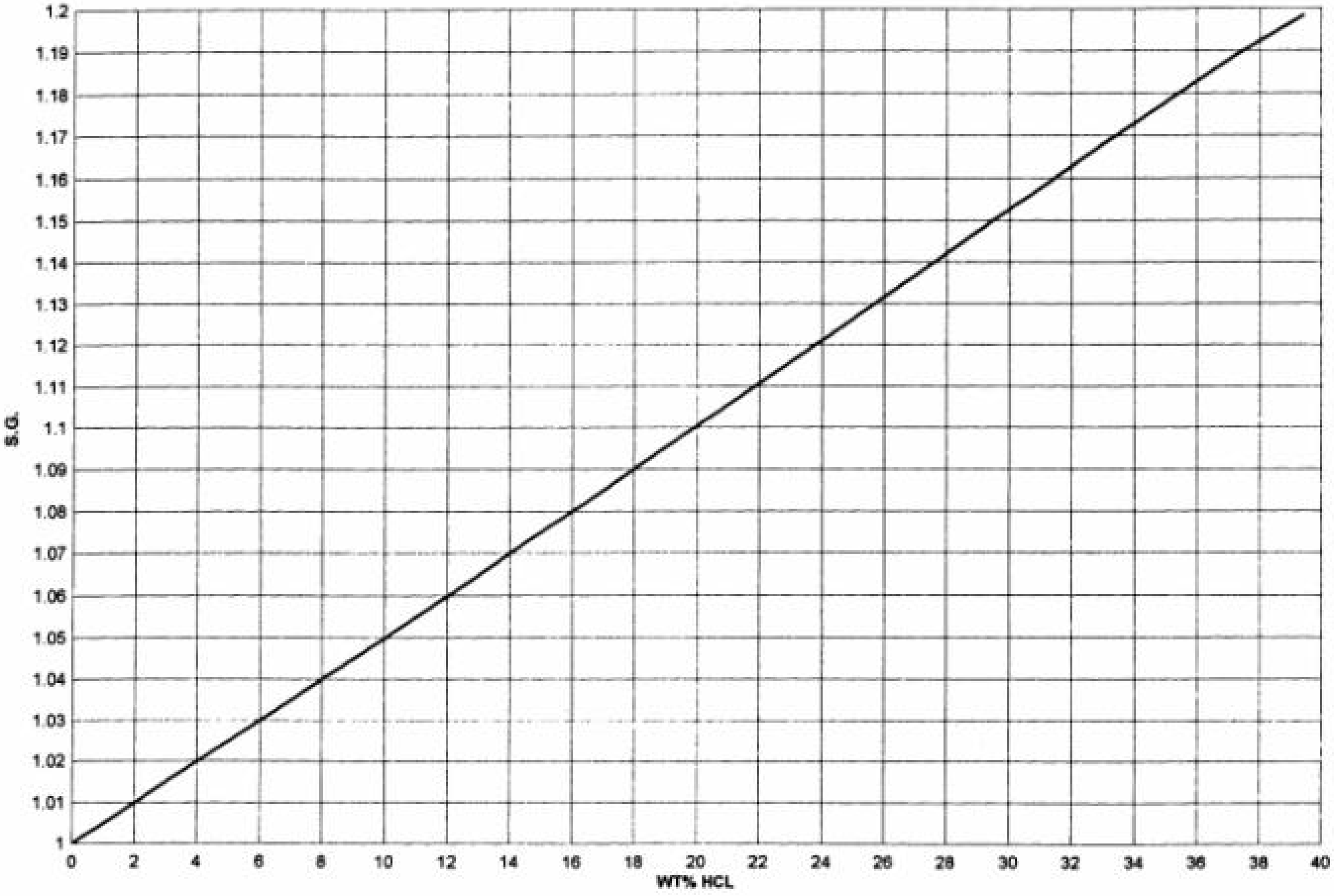
We would have a solution containing:

96 x 15.88 = 1524 lbs $FeCl_2$ (anhydrous)
\+ 96 x 2.25 = 216 lbs chemical water
1740 lbs by-products

The original water added to the tank does not take part in the reaction, therefore it is also present. The original water was made up of:

FIGURE 8

SPECIFIC GRAVITY OF HCL SOLUTIONS AT ROOM TEMPERATURE
(C.I.L. Technical Bulletin "Muriatic acid")



8750 lb solution - 875 lb acid = 7875 lb

The total weight of the final solution therefore is:

$$\begin{array}{rl} & \text{1740 lbs byproducts} \\ + & \underline{\text{7875 lbs water}} \\ & \text{9615 lbs final solution} \end{array}$$

Compared with the original solution weight, the tank has gained

9615 - 8750 = 865 lbs

Where did this extra weight come from? ... Read on.

5.2.3 *Balancing The Masses*

Let us consider the chemical equation and the fact that it must balance, and include the actual weights as calculated above

$$\begin{array}{lclcl} FeO & + & 2HCl & \rightarrow\rightarrow & FeCl_2 + H_2O \\ 72 & + & 73 & & 127 + 18 \text{ (mol wts)} \\ ? & + & 875 & & 1524 + 216 \text{ (actual wts)} \end{array}$$

The missing figure is the weight of the scale dissolved. By using our calculated difference we should then be able to balance:

$$\begin{array}{ccc} 865 + 875 & = & 1524 + 216 \\ 1740 \text{ lbs} & & 1740 \text{ lbs} \end{array}$$

We have just done what is called a MASS BALANCE based on a hypothetical case.

In essence this is what happens in a batch pickling operation. The acid is simply depleted, then the tank is dumped, a new tank is made up and the same thing is repeated again.

5.3 Pickling Several Batches

If we now look at it in terms of running steel through this tank continuously, without getting a chance to dump it on a batch basis, the obvious thing to do would be to keep adding acid also on a continuous basis at the rate it is used up.

Thus, every 96 tons of steel, we would

add 875 lbs HCl (282 gals 32% acid)

to convert 865 lbs FeO

into 1524 lbs $FeCl_2$ = 1740 lbs byproduct
and 216 lbs water

The following table demonstrates what happened to our tank over four 96 ton runs by adding 282 gals of 32% acid every batch:

starting solution		after 96 tons	after 192 tons	after 288 tons	after 384 tons
wt HCl	875	875	875	875	875
wt H_2O in HCl	1859	3718	5577	7436	9295
wt solvent H_2O	6016	6016	6016	6016	6016
wt $FeCl_2$	0	1524	3048	4572	6096
wt chem H_2O	0	216	432	648	864
total weight	8750	12349	15948	19547	23164
volume gals	1000	1278	1544	1819	2105
% HCl	10.0%	7.1%	5.5%	4.5%	3.8%
% $FeCl_2$	0	12.3%	19.1%	23.4%	26.3%
SG	1.05	1.16	1.24	1.29	1.32

Four significant changes are taking place:

The total solution weight almost tripled
The solution volume doubled
The acid concentration dropped
The ferrous chloride concentration increased

And all this only after four times 96 tons of steel pickled. Obviously we cannot continue in this manner because of limited tank capacity and because we need to maintain a certain acid strength and keep the ferrous chloride concentration at a level which prevents crystallization and fuming.

5.4 Continuous Pickling

The table in 5.3 also demonstrates that if we continue to use 32% acid, the ferrous chloride concentration increases too much too soon, which indicates we need to add more water. Obviously, this would add to the problem of tank capacity, which means we must operate under continuous overflow conditions. The overflow will contain the materials in the concentration as they are maintained in the tank. Therefore, HCl and $FeCl_2$ are continuously removed.

When there is an HCl recovery process attached to the pickling system, then these materials are converted back to acid and iron oxide. The acid comes back to be reused again but at much lower concentration than that of purchased acid due to equipment limitations in the recovery system. This is of benefit to us, since we need more water anyway, but how much more?

Assuming that the acid strength coming back from recovery is maintained at 15%, we can then operate our tank on a much more convenient basis: we simply adjust the acid flow rate, and/or the steel throughput to maintain certain conditions.

However, as we have learned before, there are definite chemical balances to be satisfied. As in every chemical process: what goes in must come out.

The table below demonstrates the relationship between acid and steel throughput and their effect on tank conditions.

EFFECT OF VARIABLE ACID AND STEEL THROUGHPUT ON PICKLE TANK

		Acid flow variable Steel Throughput Constant				Acid flow constant Steel throughput variable			
	gals 15% acid	650	750	850	950	950	950	950	950
	tons of steel	96	96	96	96	72	48	24	0
lbs	HCl	875	1010	1144	1279	1279	1279	1279	1279
material	H_2O	4958	5721	6484	7247	7247	7246	7247	7247
in	FeO	865	865	865	865	649	433	216	0
tank	HCl used	875	875	875	875	656	438	219	0
conditions	% HCl	0	1.8	3.2	4.3	6.8	9.4	12.1	15
	%$FeCl_2$	23	20.0	17.9	16.2	12.5	8.5	4.4	0
lbs	$FeCl_2$	1524	1524	1524	1524	1143	762	381	0
material	Chem H_2O	216	216	216	216	162	108	54	0
out	H_2O	4958	5721	6484	7247	7247	7247	7247	7247
	HCl	0	135	269	404	623	846	1060	1279
	total matls out	6698	7596	8493	9391	9175	8963	8742	8526
	gals overflow	650	750	850	950	950	950	950	950
	SG	1.24	1.22	1.20	1.19	1.16	1.13	1.10	1.075

From the table we can establish that under constant steel throughput:

increase in acid flow rate means
increase in acid concentration and
decrease in ferrous chloride concentration

under constant acid flow rate

decrease in steel throughput means
increase in acid concentration and
decrease in ferrous chloride concentration

In practice, this means that because the steel throughput is variable by chance only rather than by design, the acid flow rate needs to be changed, to match the steel throughput: this is best accomplished by analyzing the acid tank regularly, and making the acid adjustment to maintain conditions in the tank.

If we find by maintaining a constant acid concentration in the tank the ferrous chloride concentration remains low, we can assume based on the table studied above, that too much water is entering the system. This means that stronger acid must be introduced. On the other hand, if the ferrous chloride concentration remains high, then more dilute acid needs adding, or water should be added from another source.

If the acid flow continuously needs adjusting up and down, because the acid concentration is fluctuating, then it means that the steel throughput is also fluctuating. The problem here is of course, the starting and stopping of the steel flow. As the steel is stopped, even though it remains in the acid, no more iron oxide is dissolved, and, therefore, the acid will run through unused thus increasing the acid concentration. It is, therefore, important to stop the acid flow, whenever there is no iron oxide introduced, i.e. when the steel is stopped.

It appears that ideal conditions for pickling on a continuous basis would be approximately 12% acid and 10% ferrous chloride in the tank, which means that these concentrations are the same in the overflow.

Regardless of whether this overflow goes to be neutralized, or to be regenerated in a recovery system, it is a terrible waste of acid and energy. It stands to reason, therefore, that it is of important economical advantage to reduce the acid concentration as low as possible and increase the ferrous chloride concentration as high as possible, as in batch pickling.

The reason we would not like to do this is because it slows down pickling, can create fuming and crystallization problems. So, how can we make better use of this overflow, before it leaves the pickling process?

We can use it to pre-heat and pre-pickle the steel, before it enters the ultimate pickle tank. This is done by overflowing our original tank to another tank and another if necessary and introducing the steel first into the last of this series of overflow tanks.

This way, the steel ‘sees’ the waste acid first and the fresh acid last.

We not only use up the acid more economically, we have also increased the speed by which the steel can be pickled.

To control this system, we simply view the whole series of tanks as one giant pickle tank and aim to maintain the condition in the final overflow at as low an acid concentration and as high a ferrous chloride concentration as possible, the limits being 2% acid and 33% ferrous chloride (14.6% iron). From figures 6, 7, this acid has a vapor pressure of about 2 mm Hg, and is therefore within the usable range.

In regards to crystallization, we see on the solubility curve (figure 9), that this solution will crystallize if cooled to 50°F (10°C) and is, therefore, also well within acceptable limits.

6. **Rinsing The Steel**

After the steel is pickled, there remains a film of solution on the steel which is of the same concentration as the solution it just came out of. If left on the steel, the acid and ferrous chloride will create rust on the drying surface by chemical reactions.

This is normally referred to as flash rust or ‘stain’.

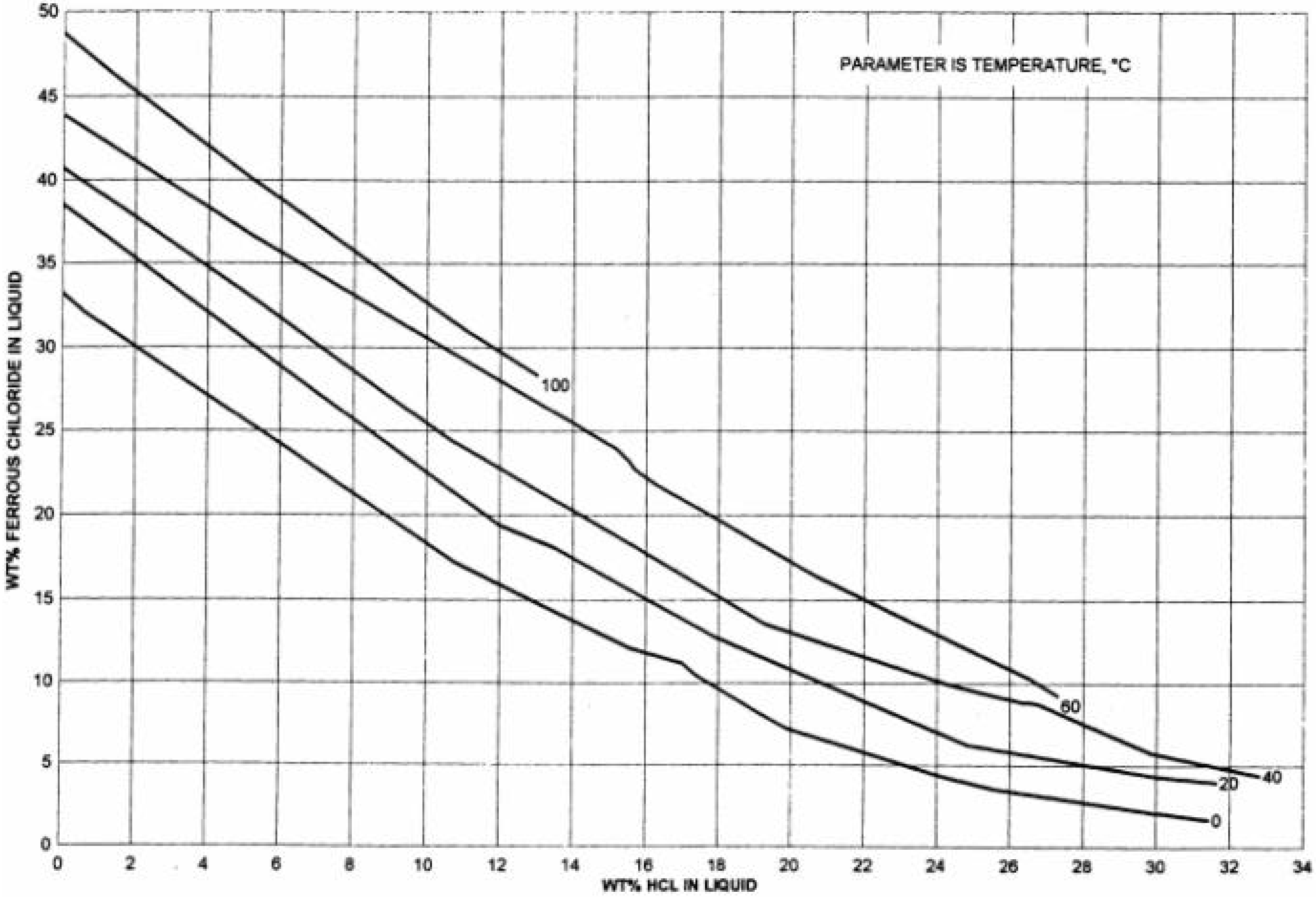
To prevent this from happening, the final pickling solution needs to be rinsed off.

6.1 Water Water Everywhere

It seems that whenever someone mentions rinsing in the pickling business, immediately everyone remembers Niagara Falls. Why? Rinsing has nothing whatsoever to do with honeymoons or even less with the amount of water going over the cliffs.

FIGURE 9

SOLUBILITY OF FERROUS CHLORIDE IN HYDROCHLORIC ACID SOLUTIONS
(Schimmel, JACS, Vol 74, #3, p4689, 1952)



However, rinsing does mean pouring water over the pickled steel or submerging the steel in water. The question is: **how much water?**

Before we go to figure this out, let us consider a few facts about rinsing pickled steel:

6.1.1 *The solution left on the steel* coming from a tank is of the same composition as the solution in that tank.

6.1.2 *Natural drainage of solution* from the steel and/or squeegying still leaves a film of solution on the steel, the volume of which is called **drag-out**.

6.1.3 *Theoretically, rinsing means replacing the drag-out* on the steel with a solution more acceptable for further processing (i.e. for drying).

6.1.4 *The volume of solution needed to rinse is theoretically* equal to the volume to be replaced. (In practice it is at least doubled.)

6.1.5 *The volume of drag-out* amounts to anywhere between one half and five gallons per ton of steel, depending on the process.

6.1.6 *Skeletons in the closet* - The most common ailment in rinsing today is what we call the 'Niagara Falls syndrome', thinking that the more water the better the rinse. The reason for this kind of thinking is the preconceived idea from way back that the more water, the less acid down the sewer, and the less acid in the rinse tank.

Let's look at this last bit of reasoning with some figures. Assuming that the drag-out from a pickle line processing 1000 tons of steel/day, is 2 gals per ton of steel and the material dragged out is made up of 10% HCl and 8% $FeCl_2$. This means right off, that 2000 gals of solution per day goes out with the rinse water. So what, you say, if we mix it with lots of water no one will be the wiser, because if you then stick some pH paper in the water going down to the river, it shows about 5 or 6 so who cares?

Well, your accounting department cares and so does the Environmental Authority. Because:

1. To dilute 2000 gal of acid to pH of 5 requires 600 million gal/day of rinse water!

2. 2000 gals at SG 1.06 = 17660 lbs
   of which 10% = 1766 lbs is HCl
   and 8% = 1412 lbs is $FeCl_2$

So accounting says: 'you are wasting 1766 x 21¢ (assumed) = $371 every day', and the Environmental Authority will say: 'all that iron eats up oxygen in the streams and the acid kills the fish and you are contaminating far too much water'.

Since we know now that by running all this water we are only camouflaging what is really happening down the sewer, then it stands to reason that by cutting back on the amount of water, something should be gained.

6.2 The Three ‘R’s’ (reduce, reuse, recycle)

6.2.1 *What To Do With The Rinse Water?*

From 6.1.4 above we see that at least 4000 gals of water are needed to rinse 1000 tons of steel; this increases the concentration of HCl and $FeCl_2$ from only ppm (as in the 600 million gals) to as much as 5% and 4% respectively, and we must realize that something should be done with this material, like, for instance, reusing it in the pickle tanks.

The accounting department will be happy and the fish will be jumping again.

To recover this rinse water, we simply collect it and let it flow to the pickle tank.

Since the HCl and $FeCl_2$ are just being returned to where they came from and at the same rate, the only thing added to the system will be the rinse water itself.

Pickle tanks always need some water addition, to make up for drag-out and evaporation, so the water content of the returned rinse can be used to maintain pickle tank level. However, the amount of water that can be added without overflowing or excessively diluting the pickle tank depends on the strength of the raw acid, and whether the tank is heated with live or closed steam (see section 7). It may not be possible to return all rinsewater to the pickle tank, but, every gallon returned is a gallon that does not have to be purchased or neutralized.

A pickle ine with no acidic effluent, and no waste treatment plant is feasible, and some such lines have been built and operated. These lines require very careful control of water consumption, and good maintenance; the rewards for this extra effort are lower operating and capital costs.

6.2.2 *The Dip rinse* is where the steel is dipped into a constantly overflowing rinse tank.

Unfortunately, the solution it is dipped into is made up of 5% HCl and 4% $FeCl_2$, created by the drag-out, if the minimum volume of water is used. Therefore, after leaving this tank, the steel must run through another tank containing cleaner water overflowing into the tank it just came out of. We can see here that we could go on adding tank after tank and never really end up putting the steel through fresh, clean water, because of the drag-out from the ‘dirtier’ tank ahead of it. In practice, plants using dip rinse usually have one or two tanks, and use a lot of water.

Using this dip rinse method is, therefore, almost impossible unless the ‘Niagara Falls syndrome’ is applied, or the clean fresh water is sprayed onto the steel, just after it leaves the rinse tank, so that the last thing the steel ‘sees’ is fresh water.

6.2.3 *The spray rinse* is a method where the last stage mentioned above is applied throughout. The collected rinse water is recirculated by pumps through spray headers, which are arranged so that the sprays have the best rinse effect on the steel. This exposes the steel to much more water in a shorter period of time in a much smaller space, than if it was dragged through dip rinse tanks.

However, the same problem applies here; the recirculated rinse water is again made up of drag-out and water, and several stages of rinsing are put in sequence, so that the water again flows counter current to the steel from stage to stage and eventually back to the pickle tank. Here again, the steel would never really be rinsed properly, unless the fresh water is applied directly to the steel, just after it leaves the last recirculating spray.

6.2.4 *Water On The Steel*

After thorough rinsing of the steel, there still remains a film of clean water on the surface. This water, if left on it too long, would invariably create rust. To prevent this, the steel must be dried and coated immediately after the rinse; for this to happen quickly, hot air is blown across the steel surfaces immediately after it leaves the rinse section. To speed this up, the steel must also be hot as it leaves the rinse.

For this reason, and because hot water rinses better, rinse systems are kept hot by live steam heating – sparging steam directly into the rinse water. The live steam condenses to form water, which increases the volume of rinsewater flowing through the system. So, to make best use of this added steam, all the heating should take place in the last rinse tank, so that this extra volume flow through all the rinse tanks (see following section 6.3), thus helping the rinsing efficiency, as well as adding heat.

6.3 Counter Current Rinsing

Figure 10 shows how a five stage countercurrent rinse system works.

6.3.1 *Cascading Means Less Waste*

As the steel leaves the pickler, it passes through squeegee rolls to remove excess solution and then enters the first spray rinse chamber. In this chamber, the water is circulated through spray headers on to the top and bottom of the strip. Now, suppose we are feeding 20 gpm of water to the rinse system, and dragging out 4 gpm of acid, containing 10% acid, 8% ferrous chloride. Then, by mixing these two together thoroughly in the spray chamber, the water will be:

$$\frac{4}{10} \times 10 = 2\% \text{ acid}$$

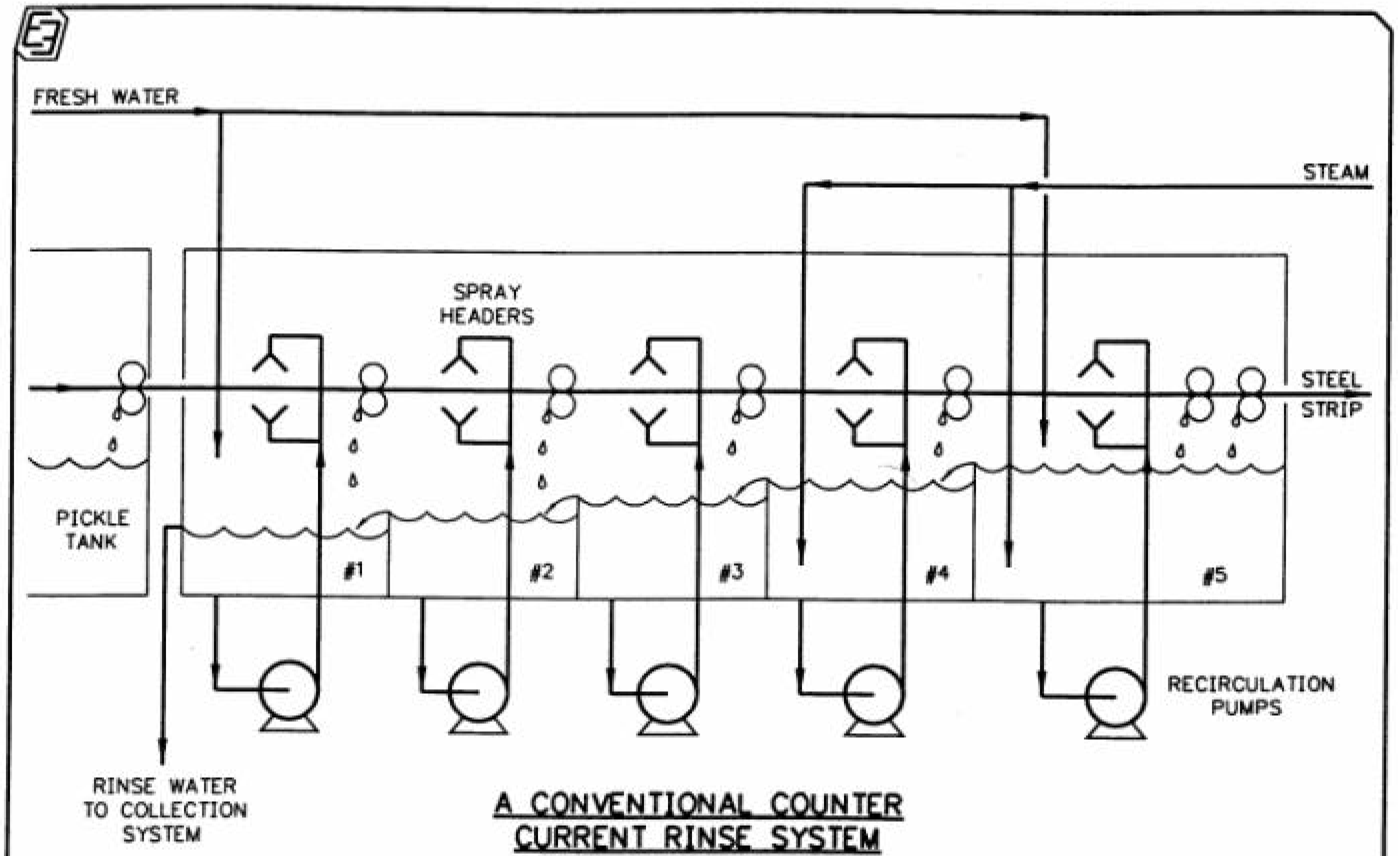
and $$\frac{4}{20} \times 8 = 1.6\% \text{ ferrous chloride}$$

After passing through the squeegee rolls, the strip drags out 4 gpm of this dirty water into chamber #2, where once again the water is mixed thoroughly with 20 gpm of incoming water. This means that the water in #2 rinse chamber is:

$$\frac{4}{20} \times 2 = 0.4\% \text{ acid}$$

and $$\frac{4}{20} \times 0.8 = 0.32\% \text{ ferrous chloride}$$

The same process takes place in rinse chambers #3, 4 and 5, and the drag out and chamber compositions get progressively weaker, as follows:



A CONVENTIONAL COUNTER CURRENT RINSE SYSTEM USING TOO MUCH WATER
FIGURE 10

	Drag In		Rinse Water	
Rinse Chamber No	% HCl	% $FeCl_2$	% HCl	% $FeCl_2$
1	10	8	2	1.6
2	2	0.16	0.4	0.32
3	0.4	0.32	0.08	0.06
4	0.06	0.03	0.016	0.012
5	0.016	0.012	0.003	0.002

This shows that the rinse water in the last chamber, which is the last water the strip ‘sees’ is very weak, and contains 0.003% acid, 0.002% $FeCl_2$ - but, it is still contaminated. To get the same result with a single dip rinse would require:

$$\frac{10\%\text{ in}}{0.003\%\text{ out}} \times 4\text{ gpm} = 13{,}300\text{ gpm of water (just like Niagara Falls)}$$

This is 665 times as much as the 20 gpm actually needed in a 5-stage rinse.

In the countercurrent rinse, the water is added to #5 chamber, and then overflows into #4 chamber, then into #3 and so on. This is arranged by having a slightly lower water level in each chamber so that as water is added to #5, it cascades over the weirs and eventually flows out of #1.

6.3.2 *The Modification That Makes The Difference*

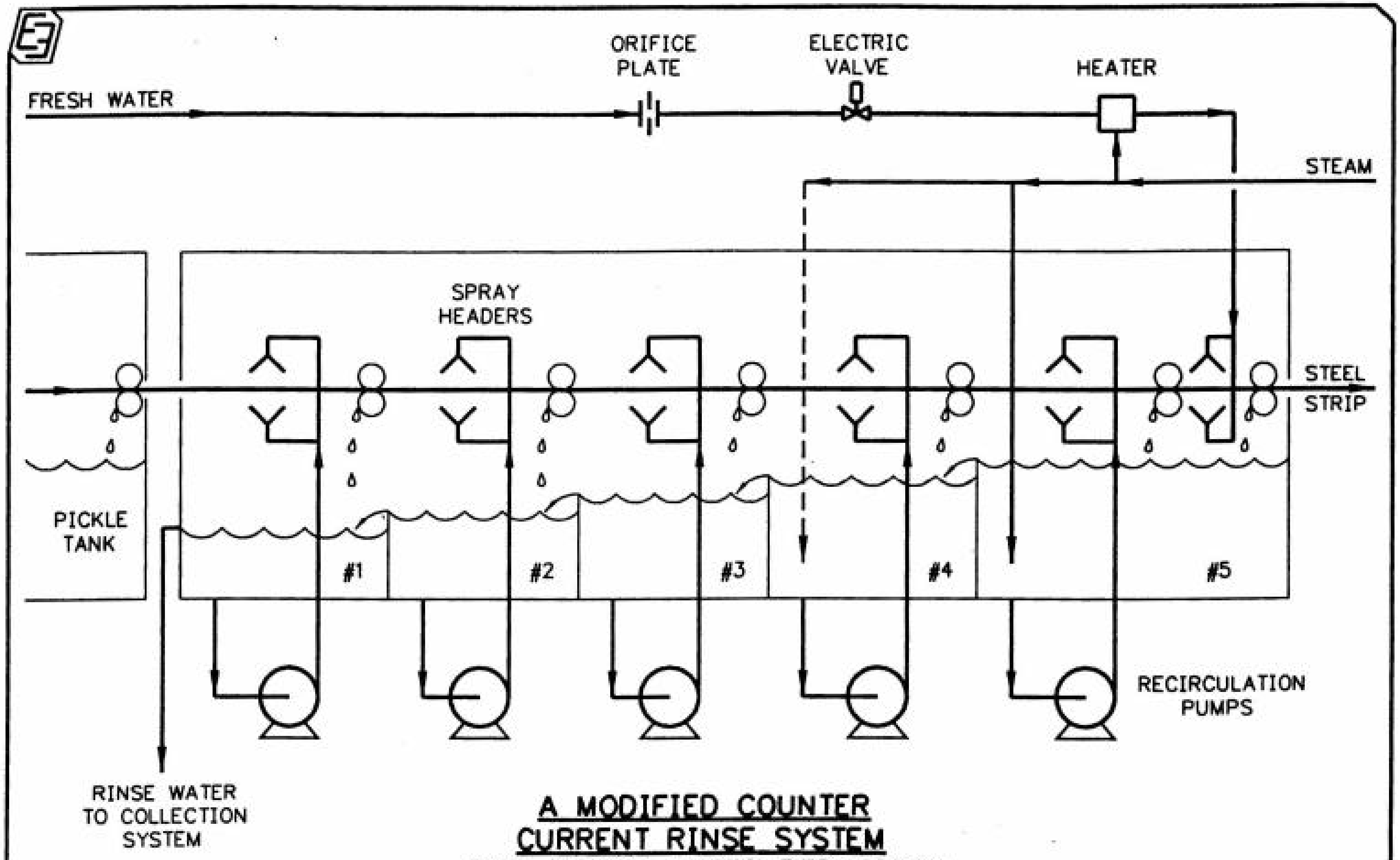
In figure 10, you see that in conventional practice, sometimes fresh water is added to #1 tank, but, based on the calculation, you would need to add 675 gpm to rinse chamber #1 to have the same rinsing effect as 1 gpm added to chamber #5 - and you have 675 gpm of effluent to process. Not only is this wasteful, but it cannot be handled when no effluent goes to the river. A modified version, as shown in figure 11, reduces rinse water production substantially by making the following changes:

- fresh warm water is sprayed on the strip just as it exits instead of being added to #5 tank
- an automatic valve shuts off fresh water when the strip stops
- an orifice plate restriction limits the water flow to 20 gpm

The reasons for these changes are apparent from the description of countercurrent rinsing above. Instead of adding clean water to a tank of contaminated water, the clean water will be sprayed onto the strip. This pushes off the contaminated water, and leaves only clean water to be dried from the strip. There is no point in spraying water on the strip when it is stationary so the automatic valve shuts off this spray when the steel stops.

Because of the limits on dirty water handling capacity, the orifice plate restriction will avoid use of water in excess of what can be handled by the total system.

Even if one complete spray chamber is out of service, it should be possible to rinse the strip with only a moderate increase in flow through the spray header; for example, with one rinse chamber out of service, an increase in flow to 35 gpm will give just as good a rinse as 20 gpm when all chambers are operating.



A MODIFIED COUNTER CURRENT RINSE SYSTEM WITH WASTE WATER REDUCTION
FIGURE 11

6.3.3 *Collecting The Waste Water*

We said above that in effluent-free pickling systems, the rinse water is used up in the pickle tanks to make up for evaporation. Sometimes, because of the complexity and size of some plants, this is done indirectly. All rinse waters are collected in one central location, and as much as possible of this water is used in the acid reclamation plant absorbers and/or for tank makeup and makeup for evaporation.

This means that it will become part of the reclaimed acid, and eventually will be added to the pickle tanks; in this way, the acid and ferrous chloride in the rinse will be reclaimed. Any excess rinse water that cannot be used in the acid reclamation will overflow and must be treated - thus not only will the acid in it be lost, but also money will have to be spent in neutralising it and removing the sludge.

By controlling the amount of rinse water to the minimum needed for quality steel pickling, the pickler operator is helping to avoid overloading the chemical treatment system and the wasting of money.

7 Heating The Pickle Tanks

7.1 Some Physics First

7.1.1 *With What?*

Heat can be introduced into a liquid by using electricity, combustion or steam. It seems that steam is the most practical and economical method to use in heating pickle tanks, because it is usually readily available, simple to operate and relatively free of maintenance.

7.1.2 *What For*

Heat is the energy introduced into the acid in the pickle tanks to:

- heat the steel going through the acid
- heat the make up acid
- make up for heat lost through the tank walls
- make up for heat lost due to evaporation

7.1.3 *What Is Heat*

Although the temperature is an indication of the quality of the heat introduced, it is not a measure of the quantity of heat. Heat is measured in BTU’s (British Thermal Units) or Calories in the metric system.

One BTU represents the heat required to raise the temperature of one pound of water by one degree Fahrenheit at atmospheric pressure.

In the metric system 1 calorie represents the heat required to raise the temperature of one gram of water by one degree Celsius at atmospheric pressure.

7.2 *Steam - A Hot Subject*

In order to realize how steam does the job of heating, we must first understand how steam is created. Steam is an intermediate between initial energy and the ultimate heat-user. This means that the heat taken from the steam when heating a tank, has to be introduced to the steam first.

7.2.1 *A Change Of State*

The natural phenomenon of changing the physical state of a substance allows us to 'load' the steam with heat and carry it to the pickle tank.

When a substance changes its state from liquid to vapor, energy is absorbed. In the case of water, this means an absorption of 970 BTU's when one lb of water of 212°F changes to one lb of steam of 212°F (at atmospheric pressure).

In other words, each lb of steam going to the pickle tank at atmospheric pressure carries 970 BTU's of heat.

7.2.2 *The Reversal*

Since the changing of the physical state of matter is equally applicable in the reverse, it follows that in order to make use of the heat carried by the steam, we must change the physical state of the steam back to water. This means that for every one lb of steam at 212°F changed to water at 212°F, 970 BTU's of heat are released to the immediate area, where this change of state takes place.

Water changing to steam is called evaporation or steam generation; the physical transformation of steam changing to water is called condensation. In practical terms this means that in order to make use of heat carried by the steam **it must be condensed.**

There are two ways to condense steam to transfer its heat into pickling solution:
- direct heating with live steam
- indirect heating by external heat transfer

7.3 In live steam heating, the steam is introduced directly into the pickling solution via a dip tube. As the steam enters the solution it is immediately condensed by the hot solution, which is cooler than the steam, thus adding water to the solution. As the steam condenses, its volume is reduced by about 840 times (at atmospheric pressure) causing a series of implosions at the end of the dip tube. This is the reason for the crackling noise usually associated with live steam heating. (If steam comes into contact with cold water in steam pipes, the same thing happens but the noisy action created here is called steam hammer, which can be damaging to steam equipment and piping).

This type of pickle tank heating is just as efficient as any other type, if the solution is continuously moved past the dip tubes, otherwise localized overheating will take place. With strip steel moving at a fast rate through the solution almost constantly in one direction, and the solution flowing at a low rate in the opposite direction, there is no question about agitation thus distributing the incoming heat evenly throughout the tank.
The only draw back of this method of heating is that water in the form of **condensate is constantly added to the pickling solution.** In effluent-free pickling this would be prohibitive: approximately 5 gals of condensate per ton of steel pickled is added using this method.

7.4 External Heating

7.4.1 *External heating means condensing steam without directly contacting the acid* by the use of a heat exchanger. By keeping a 'wall' between the pickling solution and the steam, the heat is transferred or exchanged through this wall from the steam to the solution; this causes the steam to cool and change back to water or condensate on its own side of the wall.

Again here as in live steam heating, the solution must be kept in motion constantly to eliminate overheating on the solution side of the wall. If the heat exchanger is submerged in the pickling solution, then this motion is created by thermo-static siphon action and the movement of the strip steel.

If the heat exchanger is installed outside the tank system, then the solution needs to be forcibly carried past the walls of heat transfer by circulating it with pumps from the tank through the heat exchanger and back to the tank. The circulation rate is very important in this type of heat transfer to make heating efficient. The faster the circulation rate, the better the heat transfer rate.

As explained earlier, the steam must change back to water in order to give off its heat. In the case of a shell and tube heat exchanger, the pickling solution flows through the tubes while the steam surrounds the tubes confined by the shell. The steam enters the shell at the top and if allowed to leave without changing to condensate, would do little to transfer any heat. The steam must be given a chance to make this physical transformation. This is done by restricting the outlet of the heat exchanger so that only condensate will leave the shell.

7.4.2 *Trapping Steam*

The device which accomplishes this is called a steam trap. By either mechanical or thermal means or both. This trap prevents steam from 'blowing' right through without giving off its heat, and at the same time allowing the condensate to leave, at the rate it is being produced.

Should, however, this trap fail to pass condensate, heat transfer will again be stopped, because the heat exchanger shell will slowly fill with condensate and thus eventually reduce the heat transfer area to zero.

This makes the steam trap as important in external steam heating as the circulation pump and the heat exchanger. **Steam traps are often looked at as necessary evils and thus are neglected and, therefore, account for 60% of all steam heating problems.**

7.4.3 *Temperature Control*

Regardless of the type of steam heating used, the amount of heat transferred to the solution is proportional to the volume of steam condensed. In order to control the amount of heat transferred we must, therefore, be able to throttle the flow of steam being condensed. This is usually accomplished by automated control valves, which sense the tank temperature and proportionally open or close the steam supply.

7.4.4 *Evaporation Key To Savings*

The sizing of the heat exchangers, steam supply lines, control valves, steam traps and circulating pumps is based on critical heat loss calculations made of the material to be heated. For example, the heat loss in a typical 1000 t/day pickling system breaks down as follows (in BTU's/hr)

to heat the steel	1,000,000	
to heat acid coming in	200,000	23%
losses through tank walls	1,200,000	
to make up for evaporation	8,500,000	77%
total heat loss on pickle tanks	11,000,000	

Since each lb of steam releases 970 BTU's, it follows that $\frac{11{,}000{,}000}{970} = 11{,}340$ lb of condensate must be removed from the pickle tanks every hour. This is equal to 1360 gph of water or 22.7 gpm.

As a rule of thumb, 1 lb of steam evaporates approximately 1 lb of water from the tank; we can, therefore, say that 23% or 5.2 gpm of the steam used in live steam heating stays in the tanks as condensate and thus dilutes the acid.

On the other hand, when external heating is used, all of the condensate is kept out of the pickle tanks; as a result, 77% of the water in the pickling solution evaporates, thus allowing use of contaminated rinse water at the rate of 17.5 gal/min to make up for evaporation loss.

8. Fume Control

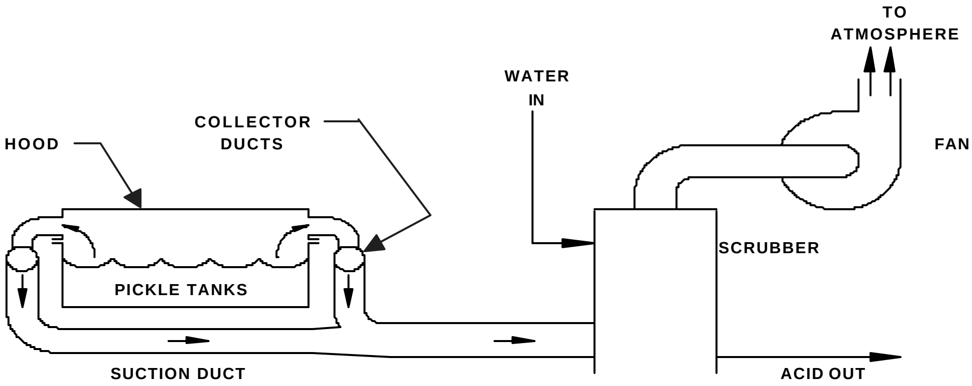
Every pickle line and acid reclamation plant operator is familiar with the tingling, acidic smell of weak hydrochloric acid, and the choking smell of strong fumes. Although hydrochloric acid is the fluid present in the human stomach, it is not natural to the human breathing system; the nose, throat and lungs. As a result, occupational health authorities limit worker exposure to 5 ppmv of hydrogen chloride gas (HCl), which is the level at which the tingling smell is just about detectable.

5 ppm is the concentration of HCl vapor over an 8% acid solution at room temperature, or a 2% solution at 140°F. If the pickle tanks were left uncovered, the HCl levels in the building would be well above acceptable limits, and conditions would be both dangerous to operators' health and have a tremendous damaging effect on the rest of the equipment in the plant.

For this reason, it is essential to have an effective fume control system on a pickle line; in the acid reclamation plant, where all vessels are closed gas-tight, such a system is not needed.

Fume control on pickle lines uses two basic techniques:
- covers on tanks, and seals on openings
- keeping the covers under negative pressure with fans

TYPICAL FUME EXHAUST SYSTEM



A typical fume extraction system consists of tank hoods, collector ducts, suction ducts, a scrubber (all working under suction), an exhaust fan and a stack to atmosphere. Most modern fume exhaust systems are made of FRP (fiberglass reinforced plastic) or polypropylene.

The fumes are controlled by drawing air from the covers to keep a slight negative pressure inside the cover. This means that, wherever there is an opening in the cover, air is drawn in from the plant, and the inrushing stream of air prevents fumes from escaping. The more openings there are, and the bigger the openings are, the more air must be removed to keep the hoods under suction and thus a larger fume exhaust system would be required; this is why the hoods are made tight and as many openings as possible are sealed or kept to a minimum size.

You may wonder why the air flow needs to be kept low - air costs nothing, and fans are relative cheap. We saw in chapter 5 that hydrochloric acid solutions give off fumes that contain both HCl and water vapor, and that these fumes get more concentrated as the acid gets stronger and hotter. For example, at a typical pickling tank condition of 10% acid, 5% iron, 180°F, the vapor above the acid contains:

0.25% HCl gas (2500 ppm) (figure 6)
45.0% water vapor (figure 5)
54.75% air

If the air is drawn across the top of this tank, two things happen:

- the vapors above the tank are carried away in the air stream and leave the pickle line with the fume extraction air. The vapors above the liquid are thus diluted.
- the liquid in the tanks gives off more HCl and water vapors to try and bring the gas above it back to the original composition

So, as more air is drawn over the liquid surface, more HCl and water vapor are swept away, and more HCl and water are evaporated. This has three bad results:

- acid which is needed for pickling is lost from the tank
- the exhaust air is contaminated with acid gas
- more heat has to be added to the tank to make up for the heat lost in evaporating the water and acid (remember from chapter 8, every pound of water evaporated required 970 BTU of heat to be added to it)

This is why the fume exhaust air flow over the tank surface should be kept to a minimum - to reduce these three problems.

The minimum exhaust rate depends on two things:

- the design of the fume exhaust hoods
- the maintenance of the fume exhaust system

Operators cannot do much about the first, but it is important to realize that prompt repairs to the fume exhaust system are needed to keep the pickle lines running well - if the system is allowed to operate with damaged equipment or broken hoods or ducts, more air has to be withdrawn to keep the fumes under control, and the wastage of acid and heat increase the cost to pickle steel.

It is possible to calculate the amount of water and acid vapors leaving in the exhaust air, but this calculation is too complicated to go into here. Normally, with efficient fume exhaust, the exhaust air should be between 120°F and 140°F and the air flow should be just enough to keep the fumes in. Under these conditions the exhaust air will contain about 200 - 500 ppm HCl gas and will evaporate about 7 lbs of water for every 1000 cubic feet of air exhausted. This means that the composition of the air leaving the pickle tank hoods amounts to approximately:

200 - 500 ppm	HCl by volume
15%	water vapor by volume
85%	air by volume

If this air were simply exhausted to atmosphere, it would create a choking cloud of gas that would affect the surrounding area, and create ‘acid rain’ that would drip on the roof of the plant, the vegetation and the houses. HCl is one of the most noticeable and unpleasant air-pollutants and was one of the first to be controlled by governments.

Environmental authorities have stringent regulations on HCl emissions. The US EPA has recently proposed rules limiting emissions to between 3 and 10 ppmv. In order to get air as clean as this, 97.5 - 99% of the HCl in the fume exhaust air must be removed. This is done by using scrubbers.

A scrubber is a device for cleaning a gas using a liquid - in most cases the gas is air and the liquid is water or a water solution. In the case of hydrochloric acid, we have already learned that HCl gas is very soluble in water, so by scrubbing the fume exhaust air with pure water, most of the acid can be removed.

To bring about the desired cleaning action, the air and water must be well mixed (it is no good just passing the air over a tank full of water) and, of course, the acidic water must be removed, as otherwise eventually it will not dissolve any more gas (it becomes saturated). The equipment used to mix the air and water is a scrubber, and there are almost as many kinds of scrubbers on the market as there are Heinz pickles - yet there are really only three basic types:

packed scrubbers	(very common)
plate scrubbers	(relatively new)
venturi scrubbers	(never used on pickle lines)

More information about fume scrubbers can be obtained by contacting ESCO Engineering.

9. **Iron Loss And Inhibitors**

One of the most important criteria in a pickling and acid reclamation operation is the iron loss. The design of the entire system is based on iron loss and the total steel tonnage. It is, therefore, important to monitor this iron loss to maintain and control efficient operation.

The iron loss is expressed in % of iron lost from the steel being pickled. To design a system, this percentage is assumed. However, by experience and past records, the assumed amount is usually quite close. In strip pickling, the iron loss is usually in the range of 0.3 to 0.5% (6 to 10 lb/ton), with the loss being highest for thin strip, lowest for heavy strip (more surface per ton on thin strip).

Great effort should be made during operations to try and reduce iron loss, in order to achieve maximum efficiency or to increase capacity.

The amount of iron lost depends on:

1) type of scale to be removed
2) amount of scale to be removed
3) length of time steel is immersed in acid
4) acid temperature
5) type of inhibitor used
6) amount of inhibitor used

Since item #'s 1 and 2 are part and parcel of the type of steel being pickled, no control can be maintained on these two items. However, item #'s 3 through 6 are relative only to plant operations, and can, therefore, be controlled as follows:

#3 do not leave steel in pickle bath any longer than is necessary to remove the scale

#4 use only the minimum temperature needed to achieve clean steel

#5 the type of inhibitor used is a trial and error determination due to the many available brands and types. It is the operator's likes and dislikes that make the difference here. However, in a recovery type system foaming type inhibitors and coal-tar based inhibitors must be avoided. Experience shows that organic types are best suited.
#6 inhibitor amounts needed are determined by practice, and monitoring the iron loss; too little inhibitor will increase the iron loss, too much inhibitor is a waste.

The actual iron loss can be calculated by knowing how much steel had been pickled and how much acid had been used or how much oxide was produced in the reclamation plant over a given period of time.

Example: 1000 tons of steel were pickled in one day and during that period approximately 5 t of oxide was produced. The oxide is chemically made up of Fe_2O_3
total molecular weight = 160
i.e. the Fe portion of the oxide is $\frac{2 \times 56}{160} = 0.7$ of the oxide
therefore 5 tons of oxide represents 5 x 0.7 = 3.5 tons iron
this means that the iron loss during that period, based on oxide production for 1000 tons of steel pickled was:

$$\frac{3.5}{1000} \times 100 = 0.35\%$$

Since the exact amount of oxide produced is not always possible to obtain, another way of calculating the iron loss is by using acid consumption figures.

This is quite a complicated calculation, because allowance has to be made for acid that is not used up, and for losses in rinse and fume exhaust.

However, it is important to become familiar with properly calculating the iron loss, because over pickling can and will affect the entire system. For instance, if the system was designed for 0.4% iron loss, this means that the reclamation plant is also designed for this capacity. Therefore, if the pickler consistently runs at more than 0.4% iron loss, the reclamation plant will not convert all the iron to iron oxide and as a result, the entire system becomes overloaded with iron, i.e. the iron analysis in the pickler will go up and up and eventually some waste acid needs to be hauled away.

By calculating the iron loss on a regular basis (see sample chart, figures 12 and 12A), say once per week, close control can be maintained on the overall efficient operation of the system, by making adjustments where necessary. Sudden increase in iron loss could mean:

- pickling times too long (line too slow)
- inhibitor dosage too low
- acid temperature too high
- heavy scale on steel

If iron loss is high, it is a good idea to try and reduce acid temperature, and maybe even run the line more slowly, but more steadily with less stops and starts.

One problem peculiar to some systems is the pickling of hot steel. In most plants, the distance between hot mill and picklers, and the amount of inventory in between ensures that all steel is cold before pickling - in fact, sometimes outside storage in the winter makes it too cold. In some plants the closeness of the picklers to the hot mill sometimes leads to steel being pickled that is still very hot at the centre of the coil. The effect of this hot steel is:

- it causes the acid to boil on the surface of the steel
- very rapid metal attack and pitting, which inhibitors cannot prevent
- extra fume losses take place due to boiling

IRON LOSS CALCULATION

Date:

Steel pickled (in 24 hours) __________tons (1)

Average acid used __________gpm (2)

Average acid concentration __________% w/v HCl (3)

Spent Acid: Average acid concentration __________% w/v HCl (4)

Average iron concentration __________% w/v Fe (5)

CALCULATION

Free acid in spent pickle liquor (line 4) = __________% w/v

Combined acid in spent pickle liquor $(\text{line 5}) \times \frac{73}{56}$ = __________x 1.3 = __________% w/v (6)

Total __________% w/v (7)

Combined acid $\frac{(\text{line 6})}{(\text{line 7})}$ = ______________ = __________ of total (8)

Total acid used (line 2) x (line 3) x 1440 x 0.0833 = ____ x _____ x 120 = __________lb/day (9)

Acid used in pickling (allowing 10% for losses) $\frac{(\text{line 9})}{100} \times 90$ = _____________ x 0.9 = __________lb/day (10)

Acid combined with iron (line 8) x (line 10) = _____ x _____ = __________lb/day (11)

Iron combined with acid $(\text{line 11}) \times \frac{56}{73}$ = ______x 0.77 = __________lb/day (12)

Iron loss (lb/ton) $\frac{(\text{line 12})}{(\text{line 1})}$ = ____________ = __________lb/ton (13)

Iron loss (%) $\frac{(\text{line 13}) \times 100}{2000}$ = $\frac{\text{\_\_\_\_\_\_\_\_\_\_\_\_}}{20}$ = __________%

Figure 12

IRON LOSS CALCULATION
EXAMPLE

Date: xxx

Steel pickled (in 24 hours)		2500	tons	(1)
Average acid used		24.0	gpm	(2)
Average acid concentration		16.0	% w/v HCl	(3)
Spent Acid:	Average acid concentration	3.0	% w/v HCl	(4)
	Average iron concentration	8.1	% w/v Fe	(5)

CALCULATION

Free acid in spent pickle liquor	(line 4)			=	3.0 % w/v	
Combined acid in spent pickle liquor	(line 5) x $\frac{73}{56}$	=	8.1 x 1.3	=	10.6 % w/v	(6)
	Total				13.6 % w/v	(7)
Combined acid	$\frac{\text{(line 6)}}{\text{(line 7)}}$	=	$\frac{10.6}{13.6}$	=	0.78 of total	(8)
Total acid used	(line 2) x (line 3) x 1440 x 0.0833	=	24.0 x 16.0 x 120	=	46062 lb/day	(9)
Acid used in pickling (allowing 10% for losses)	$\frac{\text{(line 9)} \times 90}{100}$	=	46062 x 0.9	=	41455 lb/day	(10)
Acid combined with iron	(line 8) x (line 10)	=	0.78 x 41455	=	32335 lb/day	(11)
Iron combined with acid	(line 11) x $\frac{56}{73}$	=	32335 x 0.77	=	24805 lb/day	(12)
Iron loss (lb/ton)	$\frac{\text{(line 12)}}{\text{(line 1)}}$	=	$\frac{24805}{2500}$	=	100 lb/ton	(13)
Iron loss (%)	$\frac{\text{(line 13)} \times 100}{2000}$	=	$\frac{10}{20}$	=	0.5%	

Figure 12a

This is why iron loss is high when hot steel is processed. However, there is no way of preventing the problem except by not pickling hot steel.

The most critical factor in controlling iron loss in HCl pickling is the inhibitor. The object of pickling is to remove the scale, but, as we saw in chapter 3, on chemistry, the acid also attacks the metal. We do not want this because:

- it causes etching of the steel surface
- it reduces the weight of the steel product
- it wastes acid
- it overloads the reclamation plant

Fortunately, some very effective materials called inhibitors are available to reduce the attack on the metal without affecting the scale removal. Inhibitors are very effective organic compounds which are added in low dosages, typically 0.1 to 0.3% by volume (1 to 3 gal per 1000 gal fresh acid) to the pickling acid. The inhibitor attaches itself as a film to the clean steel and prevents further acid attack; the inhibitor does not adhere to the scale.

The efficiency of an inhibitor is expressed as the percentage of base metal attack which is stopped. Thus, a 90% efficiency does not reduce the iron loss by 90% - only that part of the iron loss which is due to base metal attack.

The most economic inhibitor dosages gives about 90% efficiency. Using dosages over and above what is needed is a waste because large amounts of inhibitor are needed for very little gain in efficiency. On the other hand if dosages are too light, acid is wasted and bad product is produced.

Unfortunately, there is no sure-fire way of exactly determining the dosage requirement, except by monitoring the iron loss, as discussed earlier, a trend in relation to different dosages can be established and thus an economical dosage can be maintained.

Since there has to be a minimum average iron loss even at excessive inhibitor dosage, one simply starts pickling with a low dosage (say 1 gal per 1000 gal fresh acid) and monitors the iron loss weekly, while the dosage is slightly increased every week. The iron loss will at first be high, then gradually decrease to its minimum average level. The dosage at which this level is first reached will be the one needed. Minor adjustments to the dosage after that are made on a monthly basis. A chart kept on a weekly basis will give the necessary warning. If the high iron loss is quite critical to the operation, then of course the inhibitor dosage test can be reversed, i.e. start at high dosage and lower it weekly, until the iron loss shows a definite increase.

Choice of inhibitor really depends on secondary factors - most inhibitors have about the same efficiency of inhibition, so the specific choice depends very much on such matters as cost, availability, ease of handling, surface appearance of steel and formation of deposits. However, each time a new inhibitor is used, it is necessary to determine the dosage required by trial; thus, unless there is a very strong reason to change, it is better to use one inhibitor, and stick with it.

10. Why Acid Reclamation?

In chapter 2, discussing the change-over from sulfuric to hydrochloric acids that took place in the early 1960's, we said that one of the main reasons for making the changes was that it had become possible to regenerate, or reclaim, spent hydrochloric acid; not just the 'free' (unused) acid, but also the acid combined with the iron. This means, that, in theory, a pickler using hydrochloric acid would never need to buy any more acid once the plant had been filled initially.

Of course, no plant ever operates at perfect efficiency, so losses of a few percent have to be expected, but still the purchased acid would only be about 1 to 5% of the acid usually needed for pickling without reclamation.

To the pickler, the attractions of reclamation are:

- no spent acid to dispose of
- no worries about acid supplies in times of shortage
- oxide from the reclamation plant is easy to dispose of, and can even be a saleable product

Against these attractions are:

- another process to operate
- costs of operations

When all the figures are analysed, the actual direct cost of reclaiming acid from the spent solution is just about the same as purchased acid delivered to the plant, so the big advantage of acid reclamation and very important these days, is to **eliminate the effluent problem.** As a result, picklers have, in the past, thought of acid reclamation as a kind of waste treatment process; unwanted, undesirable and unnecessary. As we have seen already, this is not the case; acid reclamation is an important part of an efficient pickling system, and its operation must be just as important to the pickle line operators as his own pickler.

There are several proven acid reclamation processes, all using basically the same technique.

Hydrochloric acid can be recovered from spent pickle liquors because, unlike the other mineral acids, it can be vaporized and heated to high temperatures without decomposing into other, less desirable, compounds. The recovery reaction, on which all HCl recovery processes depend, is the oxidation and hydrolysis of ferrous chloride:

$$2FeCl_2 + 2H_2O + 1/2\ O_2 = Fe_2O_3 + 4HCl$$

This is a combination of the two reactions given in Chemistry (3.2.3 and 3.2.4) where it can be seen that this reaction only takes place under high temperature conditions.

There are three main reason for this:

1) High temperatures make the reaction go faster
2) High temperatures drive off the water which keeps the HCl in solution
3) At temperatures above 110°C and at normal pressures, hydrochloric acid is above its boiling point, and is, therefore, a mixture of hydrogen chloride gas and steam. Although hydrochloric acid is a very corrosive acid that rapidly attacks not only steel, but stainless steel and most other common metals, its gas, if superheated, is virtually non-corrosive to steel.

These advantages result in economics of capital cost for recovery plants, but are offset by increased operating costs, caused by having to evaporate all the water in the feed liquor (to be above the boiling point of hydrochloric acid, the system is also above the boiling point of water). Some water is needed in the hydrolysis reaction, but only 7% of the feed liquor is required for this purpose, and the remaining water in the feed has to be evaporated.

All high temperature processes use the same principle for recovering the acid from the combustion gases, (see figure 13) and for conserving water - the difference between processes lies in their reactors. There are two different types of reactors that have been developed in the past 30 years and which can be considered commercially proven in North America. These are:

spray roasters	(Ruthner and others)
fluid bed roasters	(Keramchemie)

The spray roaster is the longest established hydrochloric acid recovery system, with many successful commercial plants in Europe, and North America.

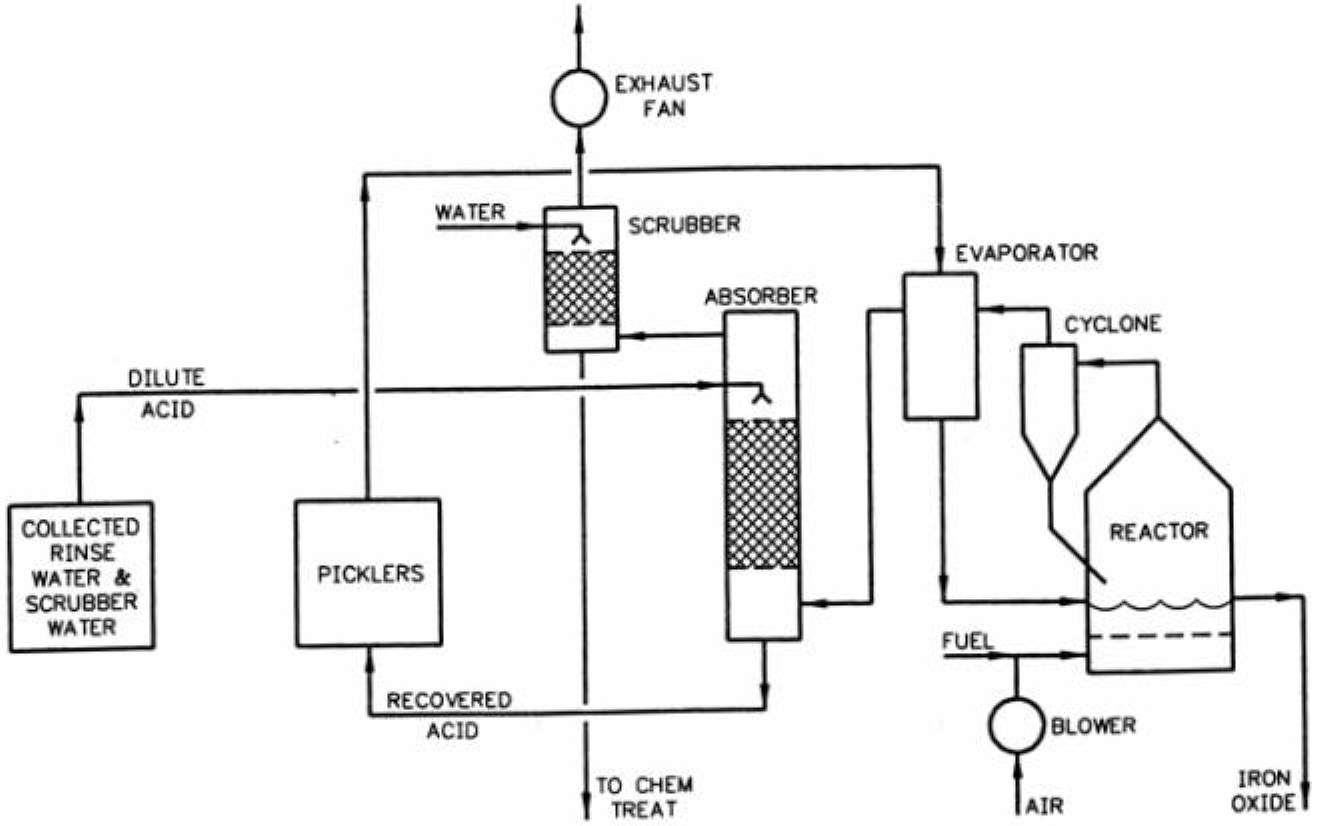
The reactor is a vertical empty tower with a cone bottom, heated by burners firing into the tower near the top of the cone. The pickle liquor is atomized at the top of the cylindrical part of the tower, and falls into the rising stream of hot gases from the burners, so that it is very quickly dried and reacted to iron oxide, which is removed from the base of the cone as a fine, light powder, made up of hollow shells, typical of a spray-dried product.

The spray roaster has the advantage of simplicity, cheapness and proven commercial performance. Its disadvantages are that the reactor is very big - between 10 and 20 cubic feet per gal, per hour capacity - and the oxide produced has a low bulk density - 25 to 40 lb/cu.ft. - which may present handling difficulties.

The fluid bed roaster, has a fluid bed, into which the waste pickle liquor, after preconcentration, is injected. The oxide remains in the fluid bed for several hours at about 800°C, and as new liquor is added, the oxide produced deposits on particles already in the bed, so producing particle growth. The oxide is removed continuously from the reactor to maintain constant level.

Because of the long residence time and high temperature, the fluid bed reactor produces a dense, coarse oxide, of low residual chloride content. On the other hand, the reactor is quite large and expensive, and more difficult to operate than the spray reactor. A number of European installations and two in N. America are in operation.

The overall thermal efficiency of the high temperature processes is about 65%, and fuel is the major utility cost and the gross heat needed is 5.85 million BTU per ton of steel pickled. Power requirement, mainly to drive air and combustion gases through the plant, is about 75 kWh for this amount of liquor, and losses of acid, due mostly to unreacted chloride in the oxide, are less than 0.5%.



TYPICAL HYDROCHLORIC ACID RECOVERY PROCESS
FIGURE 13

On this basis, the recovery cost of hydrochloric acid from spent pickle liquor is detailed in the tables based on a reclamation plant processing 5 gpm of spent acid (1000 t/day steel).

The outstanding feature of the cost table is the overwhelming importance of fixed costs. The direct cost of recovering the acid is quite low in comparison to the $130 per ton cost of fresh acid, but the fixed costs, are very high, so that the total cost is just about the same as purchased acid.

Cost of recovering 1 ton of 20° Bé hydrochloric acid *.
Plant capacity - 5 gpm spent acid.

Item	Quantity	Unit Cost	Total $/ton	
			Line	Section
<u>Raw Materials</u> Make-up acid	0.05 ton	$130/ton	$6.50	$6.50
<u>Utilities</u> Fuel Power Water	5.85 million Btu 75 kWh 400 US gal	$2.50 million $0.04 kWh $2.00/1000 gal	14.60 3.00 .80	18.40
<u>Fixed Costs</u> Operating labor Overheads Maintenance Insurance, Taxes Depreciation			29.00 29.00 8.00 3.00 16.00	85.00
Total cost per ton 20° Bé acid				109.90
Credit for iron oxide recovered 0.19 ton @$10 Contained iron				1.90
Net cost of acid recovery				$108.00

* Although the costs are expressed in terms of one ton of 20° Bé acid, the recovered acid is not 20° Bé (32%), but 18% strength. However, the plant recovers proportionately more of the weaker acid for the above costs.

The above figures are based on a system that is able to handle all the spent acid and recover it efficiently. If the volume of dilute pickle acid increases, due to low acid or iron strength, the excess spent acid has to be neutralized or hauled away, yet the acid reclamation plant costs just as much to run, even though it is not reclaiming all the acid.

More information on acid reclamation can be obtained by contacting ESCO Engineering.

11. **The Closed Loop**

Back in Chapter 2, we saw that, in order to meet government restrictions on effluents, and avoid wasting materials, it was necessary to have a complete pickling system - not just a pickle line.

Now that you have had a chance to see what goes on in all parts of the system, you can see that what happens in one area of the system affects the rest of the system and what is being done in one part of the system can be limited by other parts of the process.

For example, it is easy for a pickler operator to understand that his line capacity is limited by the speed of the line, or the rate at which coils can be changed or welded; these discussions have shown that the capacity could also be limited by the amount of spent acid that can be processed by the reclamation plant, or the volume of water going to the chemical treatment plant.

Consider figure 1C (the material balance for acid in the closed loop) and assuming a 0.4% iron loss. If the iron loss is 0.5% what can we do? One of three things:

1. Keep the same spent acid strength and volume and reduce the steel throughput from 1000 to 810 t/day.
2. Keep the same spent acid strength, but make more spent acid.

3. Increase the iron level in the spent acid.

We don't want to do 1, because the steel throughput is the most important part of the loop - it is the whole reason for having the pickling system.

We cannot do 2, because the reclamation plant cannot handle any more acid volume, so any excess spent acid will go to the chemical treatment and overload it, beside wasting acid, or be hauled away.

This means that 3 is the only answer, if steel throughput is to be maintained. The spent acid strength must be carefully controlled and watched to get the most out of the system. The pickle line operator cannot get rid of his problems any more by opening the flood gates to the river.

In fact, you know now that the spent acid strength is the single most important controllable factor in the whole system. For best system conditions, we want high iron, low acid and steady conditions in the spent acid, because:

- keeping the iron up lowers the volume of spent acid, and gives the reclamation plant higher potential capacity in terms of steel processed
- keeping the iron up and acid down reduces downtime in the reclamation plant reactors
- keeping iron up increases recovered acid strength and makes it easier to control the pickle line

What pickler operators do has just as much effect on the reclamation plant operations as what the reclamation plant operators do and vice versa. Although the acid system is critical, because there is nowhere to put excess acid, the water system (rinsing and scrubbing) is just as important. There may be a chemical treatment system, but it is expensive to run and can only take a given amount of water. Flow in excess of its capacity will lead to trouble with Environmental Authorities.

Even if equipment is installed to help reduce the total water outflow (special scrubbers and improved rinse systems) - eventually it is the hand that controls the valve which matters - the water usage must be kept to a minimum, and the only way to do this is to **use just 'enough' rather than 'plenty'**.

Remember, every time you open a valve, the material added costs money and has to go somewhere. One gpm of water too much makes an extra 1/2 a million gallons in a year of water to pump, filter, collect and clean up. Institute the three 'R's':

But first we must REDUCE before we can RECYCLE and REUSE.

12.0 ANALYSIS AND CALCULATION METHODS

There are various means of analyzing acid and iron content. The methods described below are the ones recommended and have proven most convenient for operating purposes.

12.1 Acid Determination

A known concentration of a strong base solution is titrated (measured) into a known volume of acid sample solution until the acid solution is neutralised. The amount of base solution needed to neutralise the acid is proportional to the amount of acid in the sample solution.

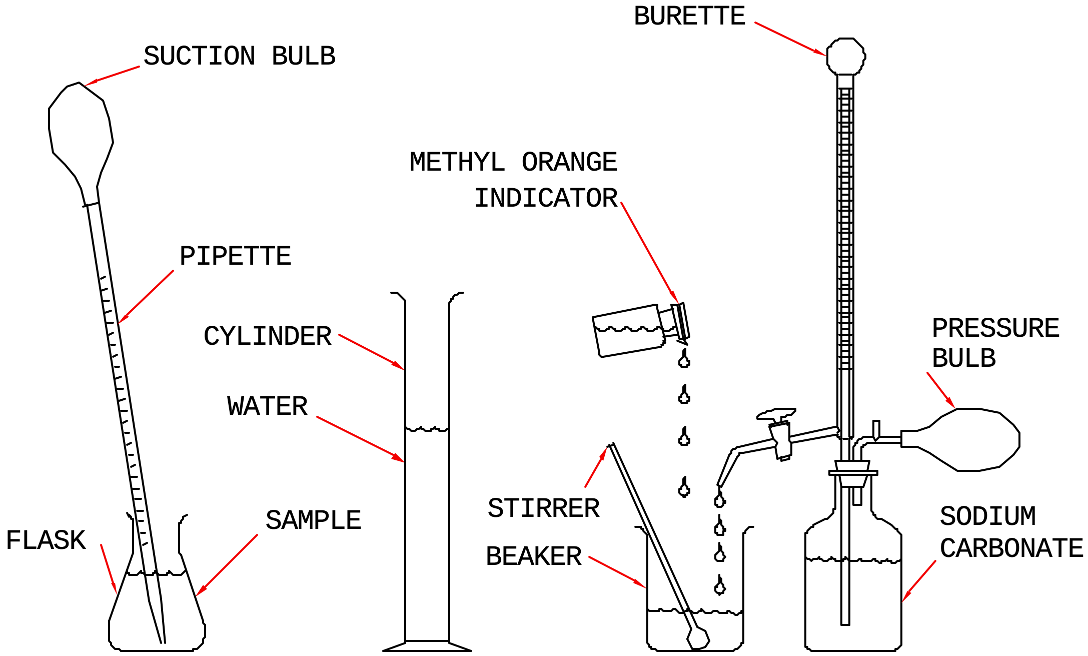
12.1.1 *Procedure*

1. Measure exactly 5 mls of sample into a 250 ml beaker
2. Add 30 to 50 mls of water (distilled if possible).
3. Add 3 to 5 drops Methyl-Orange indicator.
4. While swirling the solution constantly, titrate from 25 ml burette 1N sodium carbonate solution until a color change occurs in the solution (from red to orange).
5. Read the volume of sodium carbonate used in mls and calculate:
   mls sodium carbonate used x 0.73 = w/v % HCl.

12.1.2 *Reagent Preparation*

Sodium Carbonate Solution (1N)
Dissolve 53 grams of reagent grade anhydrous sodium carbonate in distilled water. Add sufficient distilled water to make the solution up to 1,000 ml. This makes a 1N solution.

Methyl Orange Indicator Solution
This solution can be purchased ready for use from any laboratory supply company.



12.2 Iron Determination

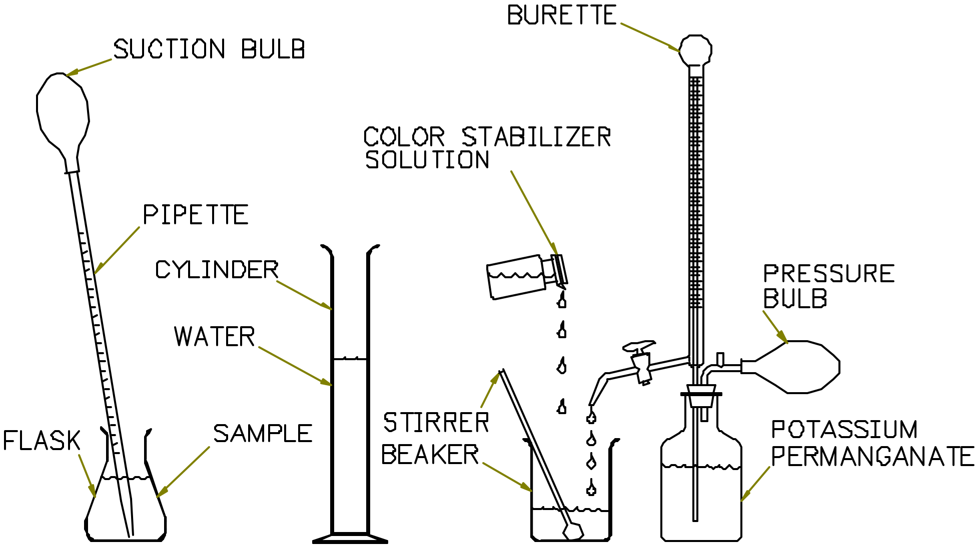
A known concentration of a reagent readily reacting with iron is titrated into a known volume of iron sample solution until all the iron in the sample solution has reacted with the reagent solution. The amount of reagent solution needed to react with all the iron is proportional to the amount of iron in the sample solution.

12.2.1 *Procedure*

1. Measure exactly 5 mls of sample into a 250 ml beaker
2. Add 30 to 50 mls of water (distilled if possible).
3. Add approximately 5 mls color stabilizer (see 5.2.2).
4. While swirling the solution constantly, titrate from 25 ml burette 1N potassium permanganate solution until the color changes in the solution (from clear to red) and remains for 30 seconds. (The solution may clear again after 30 seconds).
5. Read the volume of potassium permanganate used x 1.1 = w/v % Fe. If iron concentration is low, a 10 ml sample can be used instead of 5, then - mls potassium permanganate used x 0.56 = w/v % Fe.

12.2.2 *Reagent Preparation*

Potassium Permanganate (1N)
Dissolve 32 grams of reagent grade potassium permanganate crystals in distilled water. Add sufficient distilled water to make the solution up to 1,000 mls. This makes a 1N potassium permanganate solution. Keep from sunlight. Make up limited amounts because of short shelf life (2-3 weeks).



Sometimes the color change in this procedure is hard to determine due to cloudy conditions or poor color definition, often caused by either low acid content, high iron content or high concentration of impurities such as hydrocarbons or trace metals. To improve color change under these conditions, 5 to 10 mls of sulfuric acid solution can be added to the sample in Step 2 above. This will clear the end point for good reading of the color change. Under normal conditions the addition of sulfuric acid solution may not be necessary.

Color Stabilizer Solution
Dissolve 160 grams of manganese sulfate crystals ($MnSO_4.4H_2O$) in 1750 mls distilled water. Add 300 mls phosphoric acid and 320 mls sulfuric acid (both full strength). Stir well.

Caution: Add acids slowly to prevent splattering.

12.3 <u>Concentration Calculations</u>

12.3.1 *% Weight to Volume Method*

The analysis methods given above express the concentration analysed in % w/v, meaning that an analysis of 4% Fe corresponds to 4 g (weight) of Fe per 100 mls (volume) of solution.

For the purpose of keeping records, and maintaining the pickling process, the w/v (weight/volume) method of expressing concentrations is quite adequate; it saves time in calculating.

12.3.2 *Grams per Litre Method*

This is another way of expressing concentrations in weight to volume and is used mostly in research and quality control laboratories. The concentration is given in grams (weight) per litre (volume). One litre is 1000 ml, therefore the concentration is expressed as g/1000 ml (comparison see 5.3.5).

12.3.3 *% Weight to Weight Method*

For various specific purposes, such as accurate calculations for iron loss, crystal production, water consumptions etc., the w/w (weight/weight) concentration must be used. This simply means that the w/v concentration analysed needs converting by taking into consideration the specific gravity (SG) of the solution being analysed:

% w/v/ SG = % w/w

To use the above example in a solution of SG 1.2:

4% w/v/1.2 = 3.3% w/w

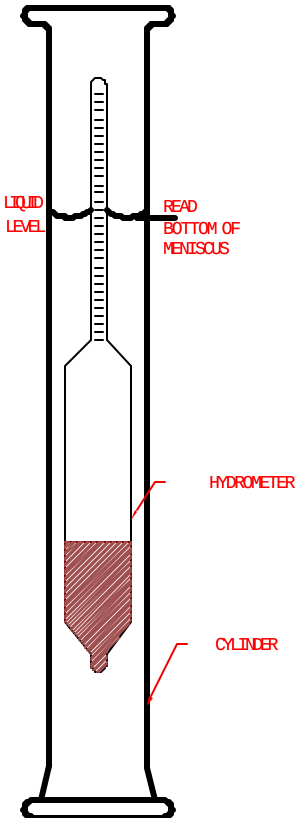
The SG of a solution is the relationship of the weight of that solution to a specific volume, using water as being 1.0. Therefore, if a container holds 10 lbs. of water, that same container would hold 12 lbs. of a solution with an SG of 1.2.

12.3.4 *Measuring the Specific Gravity:*

SG can be measured in two ways:

1. weigh a known volume of solution, i.e. if 100 ml of a solution weighs 120 g., the SG is 1.2 (water would weigh 100 g; SG 1.0).
2. use a hydrometer, which is an instrument using the fact that an object immersed in a solution weighs less by the weight of solution being displaced.

The latter method is the most common used for convenience in measurement because it gives a direct reading.



The instrument is a glass float with a calibrated stem. The float is weighted so that the glass float "sinks" vertically into the solution to be measured. The stem is calibrated so that the level to which the float sinks below the surface of the liquid corresponds to the SG of the liquid. Thus reading the scale of the stem at the surface of the liquid directly indicates the SG of that liquid.

2.3.5 *Comparison of the Three Methods:*

Assuming a solution has a specific gravity of 1.2, and the following various concentrations of a component:

- - 40 g/l is equal to 4% w/v or 3.3% w/w
- - 50 g/l is equal to 5% w/v or 4.2% w/w
- - 60 g/l is equal to 6% w/v or 5.0 % w/w
etc./ etc./

12.4 Determination of Acid or Base by pH Method

12.4.1 *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, 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 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 linear with the scale. Examples:

Sulfuric Acid (H_2SO_4):

pH 0 = 4.9 %
pH 1 = 0.49 %
pH 2 = 0.049 %
etc. (remains linear, 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 linear, behavior of salt solutions is similar)

12.4.2 *MEASURING pH*

There are two methods available to us to measure pH:

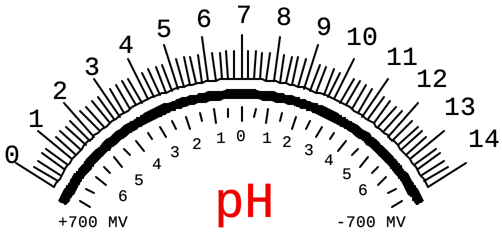
- the pH meter
- pH paper (Litmus paper)

12.4.2.1

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 (example: Battery).

The pH probes when immersed in the solution to be measured create this 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).

12.4.2.2

Using pH paper is the simplest and fastest but not necessarily the most accurate 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. A solution that does not contain water can be measured only if it is possible to add distilled water for testing.

Other ‘whys and hows’

From Esco

Whys and Hows of Sulfuric Acid Pickling

Whys and Hows of Pickle Line Fume Scrubbers

Whys and Hows of Pickle Line Waste Treatment

Visit www.esco-engineering.ca to obtain these documents.