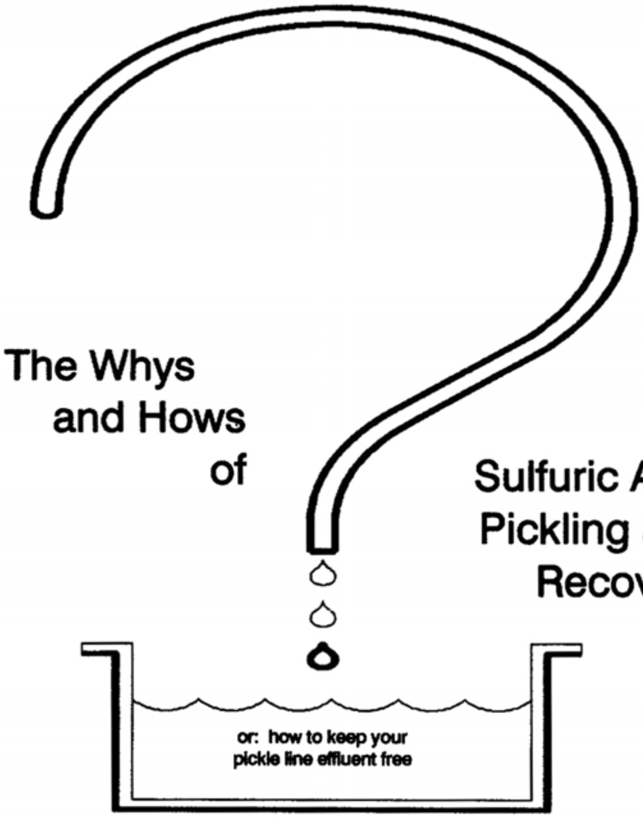
The Whys and Hows of Sulfuric Acid Pickling and Recovery



or: how to keep your pickle line effluent free

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FOREWORD

This booklet was originally published, based on ten years of previous experience, to give the pickle line operator and his foreman, supervisor and manager a fighting chance to deal with the new technological changes relating to pickle line operations.

Another ten years have passed; new technology has developed; environmental awareness has become a household word and more "hands on" experience can now be passed on to the people having to deal with the everyday problems of operating pickling and acid recovery systems. During this period we have also experienced that more or less the same recurring problems still exist in most all pickling operations and that most all of these problems can be directly or indirectly related to misunderstood pickling technology or the wrong technology applied to the wrong place at the wrong time.

For these reasons, and other lingering thorns in the sides of a lot of people, we have decided to issue this new edited 1992 edition of "THE WHY'S AND HOW'S OF SULFURIC ACID PICKLING AND RECOVERY"

As with the original edition, the intent here is still to give the people involved a fair chance to make deductions and decisions based on technologically correct facts, not based on guess work, magic, tricks or illusions!!

1.0 WHAT IS STEEL PICKLING?

1.1 The History

1.1.1 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.

1.1.2 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 metal-working 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.

1.1.3 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 - take-up systems or looping pits were added to keep the pickler on stream while the welding was taking place.

1.1.4 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 batch 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 sulfuric pickle acid into streams and rivers

Strip picklers then realise 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.

1.1.5 *The basics*

After hot rolling of steel, it is exposed to atmosphere for cooling. During this period, oxygen from the atmosphere reacts with the iron in the surface of the steel to form a crust which is made up of a mixture of the following:

FeO	- ferrous oxide	- iron oxide
Fe_2O_3	- ferric oxide	- rust
Fe_3O_4	- ferrous ferric oxide	- magnetite

This crust or scale is very brittle and very hard, almost like glass and needs to be removed before cold processing commences. It is attached to the surface of the steel in a manner which makes it very difficult to remove.

Numerous methods have been devised, to remove this scale. To mention just a few:

shot blasting
wheelabrating
scale breaking
electrolysis
pickling

"Pickling" in this context is a terrible misnomer, as it is in no way a preservation process such as is the case in food processing. The only vague resemblance would be, that both processes use acid as a means to accomplish their purpose. Since "pickling" is a well established word, both, in the food and steel industry, we must understand the definite distinction between the two:

pickling food = preservation, using acid (vinegar)

pickling steel = mill-scale removal, using acid

Failing to realise that difference could really get you into a pickle!

No preservation is achieved, when exposing steel to acid; what does happen is, that the mill scale is removed by one of two methods:

using hydrochloric Acid:	iron oxide is dissolved off the surface of the steel without any significant attack on the steel itself
using sulfuric acid:	the steel surface is being dissolved under the iron oxide, forming hydrogen bubbles which create enough pressure to pop off the scale.

1.2 The theory

Quite often the pickling process is wrongly referred to as a "cleaning" process. As we discuss the technology involved in pickling, we will discover just how wrong that reference really is.

The pickling process is in fact a chemical process and has very little to do with "cleaning" the steel. In other words, pickling does not remove anything but mill scale; if you need to remove grease or soot or whatever from the steel, don't look to the pickle tank to do it!!!

In order to appreciate the following discussion on the theory of pickling, it is helpful to be familiar with some basic chemistry. If you took high school chemistry, please read on; if not, reading part of chapter three (3.1, 3.2, 3.3 and 3.4) will be very helpful before you continue here.

The action which creates the bubbles under the scale is caused by the acid reacting with iron. This is called a "chemical reaction". Chemical reactions are expressed in equations, showing all components needed to create the reaction on the left side and all components being created on the right side of the equation. Thus the chemical reactions at work in the pickling process are expressed as follows:

Iron Oxide	+	Sulfuric Acid	=	Iron Sulfate	+	Water
(FeO)		(H_2SO_4)		($FeSO_4$)		(H_2O)
Iron	+	Sulfuric Acid	=	Iron Sulfate	+	Hydrogen
(Fe)		(H_2SO_4)		($FeSO_4$)		(H_2)

Sulphuric acid in its pure molecular state will not react with either iron or iron oxide, it must be dissolved in water in order to become reactive. It follows therefore, that these reactions only take place in aqueous solutions (in the presence of water).

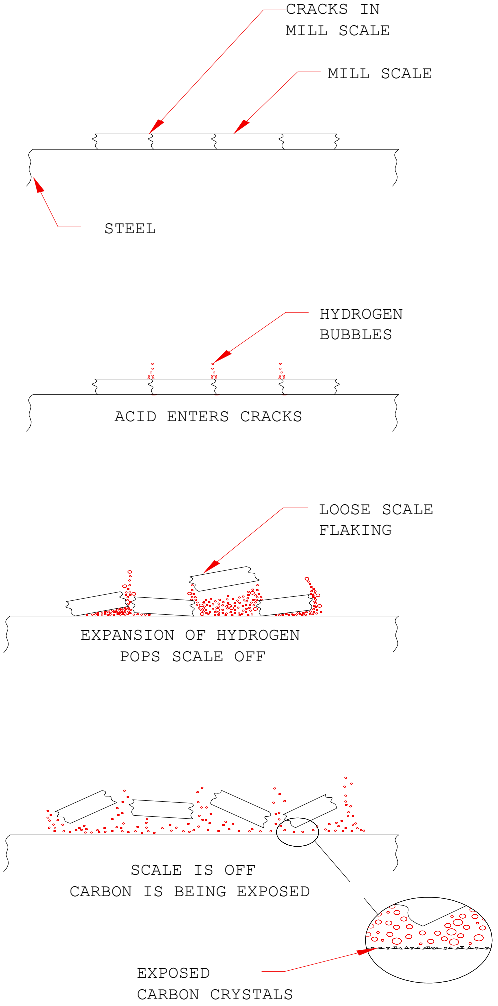
Both reactions create iron sulfate as a byproduct and both reactions are exothermic, meaning heat is created during the reaction. However, there is a distinct difference between the two in that iron dissolves quite rapidly, even violently at higher temperatures, while iron oxide dissolves very slowly or hardly at all under certain conditions.

1.3 The pickling experiment

1.3.1 What happens

If we now immerse a piece of steel covered with mill-scale in a sulfuric acid solution, we will observe the following:

- \- - bubbles form at every crack in the mill-scale
- \- - little flakes of mill-scale float off the steel
- \- - bubbles form on the newly exposed surfaces of the steel
- \- - the solution temperature rises slightly
- \- - the acid concentration is decreasing
- \- - the solution is turning slightly green
- \- - more and more mill-scale flakes are floating dispersed in the solution and are slowly settling to the bottom
- \- - finally, the surface of the steel is free of mill-scale and instead is covered in furiously dancing bubbles which are rising rapidly to the surface of the solution
- \- - an acrid odour rises from the surface of the solution
- \- - the colour of the steel changes from a bright silvery gray to a dull blackish gray
- \- - the steel is removed, the action in the solution stops, microscopically tiny particles suspended in the solution slowly settle to the bottom.
- \- - A layer of precipitate is visible on the bottom of the vessel.



The above observations accurately describe all the events taking place when steel is being pickled.

1.3.2 Why it happens

Each of the events taking place can be explained as follows: (in same order as above)

- acid is finding the steel surface through the cracks in the mill-scale, dissolving the surface iron, forming hydrogen bubbles
- expansion of the hydrogen behind the mill-scale loosens the mill-scale
- the exposed steel surface is reacting with the acid, forming more hydrogen
- heat created by the reaction causes temperature rise
- as more and more acid combines with iron, the free acid in the solution is being depleted
- the acid combining with the iron forms ferrous sulfate which is green
- because the scale does not dissolve at the same rate as iron, the loosened scale settles
- after the scale is removed, the steel continues to dissolve at a great rate, causing a continuous creation of hydrogen; the resulting furious bubbling is called effervescence
- the hydrogen bubbles breaking at the surface of the solution create a fine mist of that solution which is carried by heat convection into the surrounding atmosphere
- immediately after all the scale is removed, the surface of the steel is free of impurities and thus looks like new pure steel.

  As dissolving continues, carbon particles which do not dissolve and are part of the crystalline steel structure are exposed on the steel surface, changing its appearance to black-grey, indicating that the steel was exposed to the acid longer than needed to remove the scale
- some of the exposed carbon particles (graphite) are released into the solution by the action of the effervescence, turning the solution a dark green which clears up to a bright clear green, when the solution becomes still and undisturbed, leaving a two component precipitate:

  slowly dissolving mill-scale
  insoluble carbon dust

1.4 Temperature equals speed

During the above experiment, we would also observe, that as the temperature increased, the speed of the reactions also increased, thus indicating, that: the higher the temperature, the faster the pickling. Even though heat is evolved during the reactions, it is not sufficient to maintain ideal pickling temperature, as there is a constant loss of heat from the tank because of cold steel entering, cooling on the tank walls and evaporation of water. For these reasons, pickling tanks need to be heated.

1.5 Some serious pickling

1.5.1 The case of the disappearing acid

If we now continue the above experiment more realistically, i.e. we keep adding steel to be pickled, we would observe, that at a certain point of acid depletion, pickling will gradually come to a stop. At that point, most of the free acid in the solution will have been converted to ferrous sulfate by combining with the iron added while pickling. Thus we can conclude, that as the acid content of the solution decreases, the ferrous sulfate content proportionally increases.

By adding more acid to the solution we can continue to pickle but we must not forget that the ferrous sulfate content will continue to increase. Ferrous sulfate is actually iron salt dissolved in the pickling solution and being a salt, it has certain physical characteristics such as limited solubility. This means, that under specific temperature and concentration conditions, the solution will only hold a certain amount of dissolved salt and the excess will crystallize.

1.5.2 *Overdoing it just a bit*

Therefore, if we continue with our experiment, adding more and more iron and acid, eventually the ferrous sulfate will reach its saturation point and start forming crystals - very fine, white crystals which will settle to the bottom of the vessel and cling to anything suspended in the solution, including the steel being pickled. This prevents the acid from dissolving the iron properly, thus slowing down the pickling action. In addition, the settled crystals form a cohesive mass (almost like cement) which is very difficult to redissolve. These white crystals are called "ferrous sulfate monohydrate".

1.5.3 *What, where, when : The waste acid dilemma*

Considering this observation, we would be well advised to discard the pickling solution and start with a new solution well before this adverse condition develops. However, when we think about "dumping" the used solution, we have to remember, that the only reason for dumping it, is because of the accumulated ferrous sulfate. If we could just remove the ferrous sulfate, pickling in the unused free acid could continue, which is exactly what a recovery system would do. But, because we do not have that convenience in our experiment (or in pickling systems without acid recovery) a lot of unused free acid would also be dumped. Therefore, before the crystal condition is reached, we stop adding acid and continue pickling, until the minimum acceptable acid concentration is reached, **then** we dump; economically sound and environmentally more acceptable.

1.6 Let's get practical

Having observed the chemical pickling in action, we now must apply the physical parameters necessary to make the process work in practice. The following are ideal ranges of operating conditions within which all sulfuric acid pickling systems can be operated. Exact parameters cannot be listed, as local conditions and individual preferences must be considered.

Acid concentration	8 to 14% w/v
Maximum iron concentration	8 to 10% w/v (consult the solubility chart in Chapter 2)
Solution temperature	160 to 180°F
Immersion time	judged by results experienced and noted (depending on surface condition and type of mill-scale)
Minimum acid concentration	actual plant experiments indicate that in some instances, pickling is still possible at 3% acid

2.0 WHAT IS ACID RECOVERY?

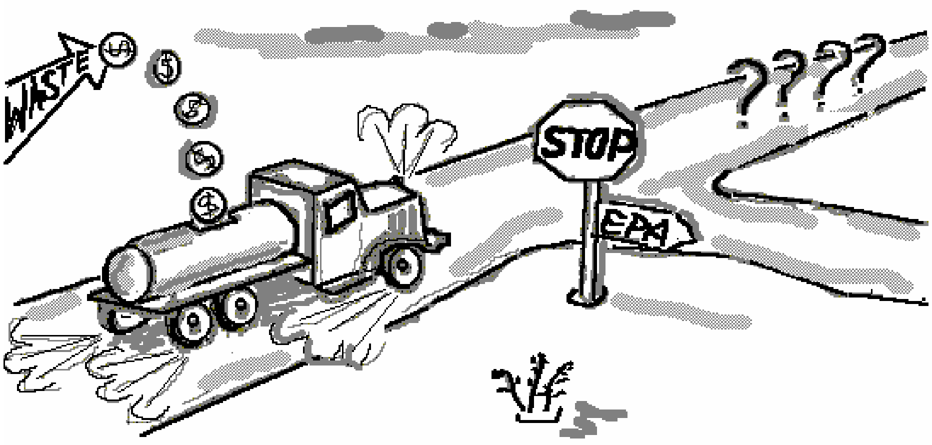
2.1 A Matter of HAULAGE

There are three ways of handling waste acid (sometimes also referred to as spent acid):

- Hauling it away by a licensed disposal company
- Treating it in a waste water treatment system and hauling away the resultant sludge
- Passing it through an acid recovery system, selling the resultant byproduct and re-using the recovered acid

Only economic assessment will determine which of the three methods is the most appropriate. Such facts as the size of the operation, the reliability of haulage, the proximity of disposal facilities, space availability, local State, Provincial or Municipal regulations etc. also play an important role. Regardless of the method used, something needs to be **hauled** away.

Even in the case of acid recovery, it is very important to remember, that a byproduct is produced which also needs to be hauled away. This byproduct is ferrous sulfate heptahydrate which is a green loose crystal just a bit coarser than cooking salt. During the recovery process these crystals are produced by lowering the temperature of the spent acid, thus effectively removing dissolved iron from the acid. The resultant recovered acid, although still containing some, but substantially less, dissolved iron is re-heated and re-used for further pickling.



The following discussion explains what actually happens during acid recovery in as much detail as practical.

2.2 The SALT is the key

Recovery of acid in this case means removal of accumulated unwanted byproduct from the acid solution being used for pickling, the unwanted byproduct being ferrous sulfate, or iron salt. One of the physical characteristics of dissolved salt is, that it will crystallise under certain specific temperature/concentration conditions. During pickling, this characteristic is a definite hindrance; however, the same characteristic is the basis of the process which can remove the ferrous sulfate from the pickling solution.

2.2.1 *CHARTING the salt*

Scientific experiments have shown that, depending on certain conditions, this salt will form one of two types of crystals:

FERROUS SULFATE MONOHYDRATE $FeSO_4.H_2O$	contains one molecule of water, (a very fine white precipitate)
FERROUS SULFATE HEPTAHYDRATE $FeSO_4.7H_2O$	contains seven molecules of water, (a coarse clear green crystal which can grow to any size)

The condition at which the crystals change from the one type to the other is called the phase change. Based on the experiments, a chart was developed to show fairly accurately under what conditions each type of crystal is either soluble or insoluble in water. Because this change takes place as a result of the solubility of ferrous sulfate, the chart primarily indicates it's solubility under all possible acid, iron and temperature conditions.

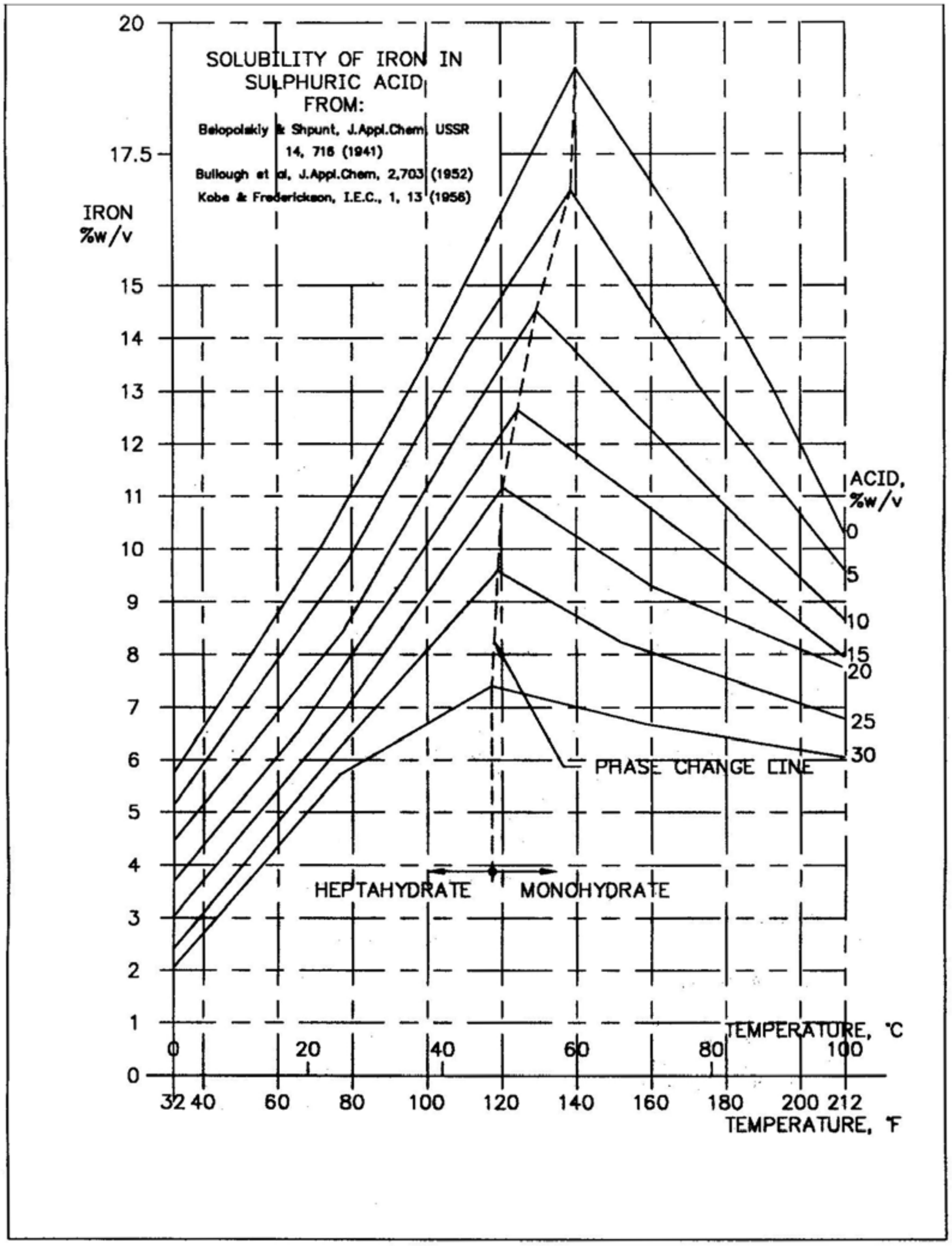
2.2.2 *Throwing CURVES*

Looking at the solubility curve, we can see, that three separate conditions determine the state of solubility: solution temperature, acid concentration and ferrous sulfate concentration (expressed as iron). Also we can see that the curves come to a definite peak; the line connecting these peaks is the phase change line.

At this point, let us observe another experiment using the same pickling solution from the previous experiment just prior to dumping it. Assuming that the solution is at 180°F, 10.8% iron and 10% acid. To find out how this solution relates to the solubility curve, follow this procedure:

- draw a vertical line at 180°F
- note where this line intersects with the curve representing 10% acid
- draw a horizontal line from this intersection to the left
- note where this line intersects with the iron scale: 10.8%

To find out, what significance this has on our experiment, we must know more about how to interpret the solubility curve:



SOLUBILITY OF IRON IN SULPHURIC ACID FROM:

Belopolskiy & Shpunt, J.Appl.Chem. USSR 14, 716 (1941)

Bullough et al, J.Appl.Chem., 2,703 (1952)

Kobe & Frederickson, I.E.C., 1, 13 (1956)

2.2.3 Making SENSE of the curves

- if the point of intersection between the temperature line and the acid curve is to the right of the phase change line, monohydrate will be formed at that level of iron concentration
- if the point of intersection between the temperature line and the acid curve is to the left of the phase change line, heptahydrate will be formed at that level of iron concentration
- if the analysed iron concentration is at or above the iron concentration indicated by the intersection between the temperature line and the acid curve, crystallisation is taking place
- if the analysed iron concentration is below the iron concentration indicated by the intersection between the temperature line and the acid curve, the ferrous sulfate remains dissolved
- the % acid curves must be considered as average centres of fairly wide bands following the curves, thus the results of any readings from these curves must be considered as guide lines to operate by, rather than accurate operating data.

Based on these facts, our experimental pickling solution is either forming monohydrate or on the verge of doing so. From our previous discussion, we know that this is not a good position to be in when pickling, i.e. we should have pickled at a lower acid concentration or lower temperature or stopped pickling at a lower iron level. Now examine these "should have's" on the solubility curve, in particular the one about the temperature:

2.3 CHILLING down

If we were to lower the temperature of our solution, (you can simulate this by aligning a straight edge with the temperature line at 180°F and moving it slowly to the left) you will note, that as the temperature goes down, the intersection with the acid curve goes up along the curve thus indicating that the allowable iron concentration increases. this means, that crystallization of monohydrate does not occur at 10.8% iron and 10% acid if the temperature is below 180°F (something to think about when pickling).

If we now continue to lower the temperature, you will find, that suddenly, the acid curve starts going down again. It does this at the phase change line. This means that we are entering heptahydrate territory and that if we arrive at a crystallisation condition now, the crystal will be in that form. Now let us do this with our experimental solution:

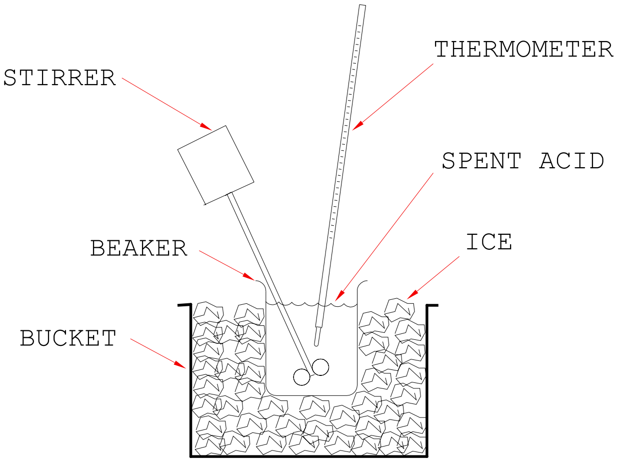
2.3.1 Clouds of MOLECULES

Assume we can lower the solution temperature slowly while stirring it continuously (e.g. by packing the container in ice) you will find that nothing significant happens until the temperature reaches 95°F. At that point, the appearance of the solution changes from clear green to cloudy green, indicating, that nucleation (formation of the crystal molecule) has taken place. By checking on the solubility curve we find that this is where the 10% acid curve intersects with the 10.8% iron line. Analysis of the solution at this point would confirm this.

If we continue to analyse the solution, as the temperature is being reduced, we will observe, that our analysis will match the iron concentration at any given point of temperature on the acid curve. this means, that the difference between the original analysis and the analysis at any point below 95°F represents ferrous sulfate that came out of solution and has crystallised.

2.3.2 A GROWING experience

In our experiment we will note, that the cloudiness of the solution slowly gives way to clear with cloudy patches which means that the heptahydrate crystals are growing as the temperature is falling. Assuming, that we can reduce the temperature to 40°F we can therefore determine on the solubility curve (intersection between the 40°F line and the 10% acid curve) that all the iron in the original solution EXCEPT 5.1% has converted into hepta hydrate crystals.

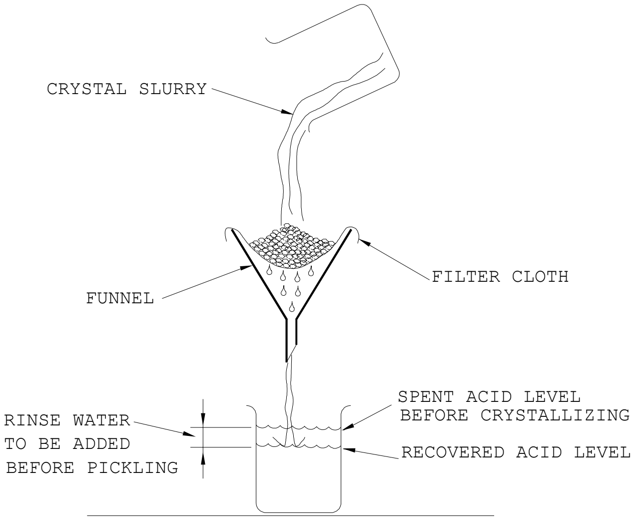


By studying the solubility curve, you will see that even more heptahydrate will be formed if we increase the acid content of the solution. By adding the acid needed for making up the next pickle tank just before we start crystallizing, we can remove more crystals in the recovery process.

Cooling to a lower temperature is not usually practical, but if it can be done, even more iron is crystallized. A word of warning however, at below 30°F and certain acid conditions, ice crystals will form, thus creating a mixture of ferrous sulfate crystals and ice. This ice will tie up some of the free acid, then melt when the crystals are stored at ambient temperature. Then the tied-up acid is released and some of the crystals will dissolve because of the molten ice, causing a highly acidic runoff under the crystals.

2.4 SEPARATING the salt

If we stop stirring the solution after cooling to 40°F, we will observe that the green crystals quickly settle to the bottom, leaving a clear green solution above.



By pouring this mixture of liquid and crystals through a strainer, we will have successfully removed nearly half the dissolved iron from our pickling solution which after straining is called: Recovered Acid. On examination of this recovered acid, we find that its volume is much less then that of the spent acid we started with. What happened,- did we spring a leak ? Well almost, in effect however we lost quite a bit of water by removing the crystals, not as wet water clinging to the surface of the crystals, but rather as part of the solid crystal.($FeSO_4$. $\mathbf{7H_2O}$)

2.5 Overcoming the WATER-SHORTAGE

If you recall, the crystals we removed are chemically made up as ferrous sulfate heptahydrate and it is in the heptahydrate portion where we can find our lost water. The amount involved can be accurately determined, but that's a subject for one of the following chapters, let it suffice to say at this point, that the amount is quite substantial. This means that because of the loss of that water, the concentration of acid and iron in the recovered acid is slightly higher than the solubility curve would have us believe. Therefore, before we can re-use the recovered acid, we must add enough water to it, to make up for the loss. **What a clever opportunity to use up the acidic rinse water from pickling instead of having it neutralised in a costly treatment system!!**

How much water to add? Rather than calculating this, in reality all we have to do is add water, until the loss in volume is made up e.g. top up to where the liquid level was, before the crystals were removed, then re-heat it back to pickling temperature and -- presto, we can pickle again.

2.6 The SIMPLICITY of it all

-- We pickle steel in sulfuric acid all the while making ferrous sulfate

-- We pickle until the ferrous sulfate concentration reaches the maximum allowable under circumstances dictated by the operation

-- We cool the resultant spent acid, all the while making ferrous sulfate crystals

-- We cool until the lowest possible temperature is reached

-- We separate the resultant crystals from the acid

-- We add water to make up for volume lost

-- We re-heat the resultant recovered acid

-- We start all over again.

The above of course is the basic description of a typical batch process. There are also acid recovery systems available and in operation, which work on the basis of continuous processing. Although their physical operating procedures are quite different, the basic theory as described above is exactly the same (see "CONTINUOUS ACID RECOVERY").

3.0 CHEMISTRY

3.1 Just the FACTS and nothing but the Facts

Carbon rings, valences, atomic numbers, electron orbits !?? Does all this sound familiar ? No ?-- then do not worry, we will not go into all that.

Although this is a very complex subject, we will make an attempt at discussing just enough of the facts so that you may become familiar with the basic technological reasoning behind the design and operating parameters of pickling and acid recovery.

3.2 The ATOM, nature at it's tiniest

Matter as we know it is made up of protons, neutrons and electrons which together make up the smallest form of matter called the ATOM. All matter on this earth is made up of specific atoms. In order to be able to distinguish between the different atoms, they were given names such as "Oxygen", "Hydrogen", "Sulfur". Because chemistry as a science started developing in the age when Latin was a common language, some of the atoms still bear names such as "Ferrum", "Argentum" or "Plumbum" , which translates into: iron, silver and lead. To make it simpler to distinguish these atoms in calculations, texts and so forth, abbreviations of the names are commonly used, like O = Oxygen, H = Hydrogen, S = Sulfur, Fe = Iron, Ag = Silver, Pb = Lead.

3.2.1 A weighty problem

Further, to distinguish between the different atoms in terms of their physical properties, a weight relationship was established, using the lightest atom as the base. Hydrogen is the lightest atom, therefore it was given the atomic weight of 1. This means, that the atomic weights of all other atoms will be expressed as to how many times heavier they are than hydrogen. All of this data and much more is compiled in the "PERIODIC TABLE OF THE ELEMENTS" (see page 17) to make it relatively simple to find out, for instance, that the atom Fe (iron) is 56 times heavier than the atom H (hydrogen). Please note, that for the purpose of any calculations relating to pickling and acid recovery, we are rounding off the atomic weights to the nearest whole number.

3.3 The MOLECULES, togetherness

The laws of nature prevent some of the base elements as described above to appear as matter in their atomic form, because they are reactive as single atoms. This is why, for instance, O (oxygen) never appears by itself. In order for it to be stable, it looks for another atom to link up with. Under certain circumstances, it simply links up with another of it's own atoms, forming the double atom we know as oxygen gas. The same is true with H (hydrogen), where the double atom forms the gas known as hydrogen.

If physical circumstances allow it, the reactive single atoms will also link up with other reactive atoms such as, for instance when a single O links up with two H, which gives us a triple atom HOH known to us as H_2O or water. Whenever this linkup or marriage between atoms occurs, the resulting combination of atoms is then called a MOLECULE such as O_2 oxygen gas, H2 hydrogen gas, H_2O water.

Note, that the number of atoms is distinctly expressed in the abbreviated notation of the molecule. Often these numbers are taken from the Greek, for instance:

CO_2 - Carbon **di**Oxide = two oxygen atoms attached
CO - Carbon **monO**xide = one oxygen atom attached
$7H_2O$ - **hepta**Hydrate = seven molecules of water
H_2O - Hydrogen **mono**xide = one molecule of oxygen attached

For your reference, some Greek numerals:

1	2	3	4	5	6	7	8
mono	di	tri	tetra	penta	hexa	hepta	octa

3.3.1 *Gaining weight*

As the atoms combine to molecules, so do their atomic weights. Each molecule therefore carries a molecular weight equal to the sum of the combined atomic weights. For instance: H_2O, water has a molecular weight of 1+1+16 = 18. Oxygen has a molecular weight of 16+16 = 32. Hydrogen has a molecular weight of 1+1 = 2. The weight relationship of molecules therefore is the same as discussed above, the base being the atomic weight of hydrogen, i.e. the molecule water is 18 times heavier than the atom hydrogen.

3.4 Let's get PRACTICAL

Armed with this tremendous amount of knowledge, we can now try to make some sense out of how and why pickling and acid recovery systems are designed in the way they are.

3.4.1 *The balancing act*

In nature, everything that happens has to balance out somehow. It's no different in chemistry, in fact balancing chemical reactions is what chemistry is all about. Take for instance one of the reactions taking place in pickling:

Iron	+	Sulfuric Acid	=	Ferrous Sulfate	+	Hydrogen
Fe		H_2SO_4	=	$FeSO_4$		H_2

To assure that this equation is balanced, we must apply the atomic weights to all the atoms and molecules in the equation: (see periodic table).

	ATOMIC WEIGHTS	MOLECULAR WEIGHT
Fe	56	56
H_2SO_4	1+1+32+16+16+16+16	98
$FeSO_4$	56+32+16+16+16+16	152
H_2	1+1	2

WebElements: the periodic table on the world-wide web

http://www.webelements.com/

Key:

element name
atomic number
symbol
atomic weight (mean relative mass)

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.066	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [97.907]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [208.98]	astatine 85 **At** [209.99]	radon 86 **Rn** [222.02]
francium 87 **Fr** [223.02]	radium 88 **Ra** [226.03]	89-102 **	lawrencium 103 **Lr** [262.11]	rutherfordium 104 **Rf** [261.11]	dubnium 105 **Db** [262.11]	seaborgium 106 **Sg** [266.12]	bohrium 107 **Bh** [264.12]	hassium 108 **Hs** [269.13]	meitnerium 109 **Mt** [268.14]	ununnilium 110 **Uun** [272.15]	unununium 111 **Uuu** [272.15]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]		ununhexium 116 **Uuh** [289]		ununoctium 118 **Uuo** [293]

*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [144.91]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
**actinoids	actinium 89 **Ac** [227.03]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237.05]	plutonium 94 **Pu** [244.06]	americium 95 **Am** [243.06]	curium 96 **Cm** [247.07]	berkelium 97 **Bk** [247.07]	californium 98 **Cf** [251.08]	einsteinium 99 **Es** [252.08]	fermium 100 **Fm** [257.10]	mendelevium 101 **Md** [258.10]	nobelium 102 **No** [259.10]

Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - http://www.iupac.org/). Names have yet to be proposed for the most recently discovered elements 110–112, 114, 116, and 118 so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings aluminum and cesium are normal while in the UK and elsewhere the common spelling is sulphur.
Group labels: the numeric system (1–18) used here is the current IUPAC convention.
Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 1997 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable nuclides and are represented by the element's longest lived isotope.
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Therefore, back in the formula, substituting symbols with molecular weights:

Fe	+	H_2SO_4+	=	$FeSO_4$	+	H_2
56	+	98	=	152	+	2
		154	=	154		

The equation is balanced

3.4.2 Playing the numbers

Because atomic weights are all related to base 1, in practice they can be given actual weight units (provided the same units are used throughout each equation). We can therefore determine exactly how much of each component in the reaction is required or produced i.e. from the above balanced reaction we can determine:

> it takes 56 lbs of iron and 98 lbs of sulfuric acid to produce 152 lbs of ferrous sulfate and 2 lbs of hydrogen

Please note, that the weight ratios expressed in chemical equations are theoretical and need to be adjusted for the following reasons:

a. the chemicals used in practice are hardly ever pure or in full strength
b. in order for a reaction to occur, one of the components in the equation must appear in excess otherwise the reaction would take forever to complete.

3.4.3 Making it work for us

These weight ratios are the basis of the material balances the engineer produces to design equipment. As an example, let us say, that a plant pickles enough steel in one week to dissolve 1000 lbs of iron. Using the above equation we can deduce the following:

pure sulfuric acid required	1000/56	x	98	=	1750 lbs
pure ferrous sulfate produced	1000/56	x	152	=	2714 lbs
pure hydrogen produced	1000/56	x	2	=	36 lbs

(56,98,152 & 2 are the respective molecular weights appearing in the equations)

Besides these facts, we also know, that sulfuric acid as purchased has a concentration of 93% and weighs 15 lbs/USG (approximate figures) and we also know, that the ferrous sulfate is removed as heptahydrate. Thus the following adjustments need to be made to the above material balance:

Actual commercial acid to be purchased for a one week period would be

1750/93x100 = 1882 lbs or 1882/15 = 125 USG (105 IG)

To determine the actual ferrous sulfate produced as heptahydrate crystals we first need to apply molecular weights to the formula:

IRON SULFATE.HEPTAHYDRATE
$FeSO_4.7H_2O$
Molecular weights: 152 + 126 = 278

Actual ferrous sulfate heptahydrate crystals produced: 1000/56x278 = 4964 lbs

Water contained in the crystals: 1000/56x126 = 2250 lbs

Now you can understand how all that water disappears during crystallising !

3.5 Pound for pound, a simple MEASURE

After absorbing all of this valuable information, we can now draw some simple conclusions about what makes pickling and acid recovery tick by way of chemistry:

- - the chemical formulae allow us to "see" the reactions

- - the atomic and molecular weights allow us to "feel" the reactions

- - the conversion to weight units allows us to "measure" the reactions

It is always a good idea, to convert a measure to it's lowest common denominator for realizing the significance of that measure compared with known units. Looking at the above calculations, and by reducing the results to be related to 1 lb of iron dissolved, we can make the following statement:

For **every one pound** of iron dissolved:

1.75 lbs pure sulfuric acid is required
5.0 lbs ferrous sulfate heptahydrate crystals are produced
2.3 lbs water needs to be added to the recovered acid

Now, in order for the engineer to design equipment for any pickling/acid recovery operation, all he needs to know is: "How much iron is dissolved in the pickling process on a daily basis", i.e. what is the **iron loss** in the process.

4.0 WHAT IS IRON LOSS?

4.1 A question of capacity

In order to size equipment and decide how to operate a system, both the engineer and the operator must know what determines the operating capacity of a pickling/acid recovery system. There are two capacities to be considered:

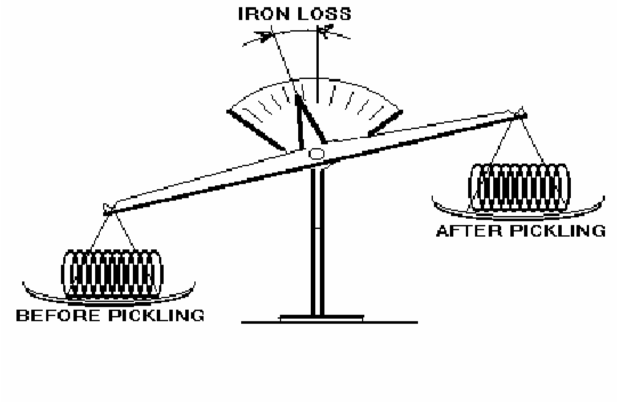
- the steel capacity
- the chemical capacity

Both are equally important and both are dependent on one another. The steel capacity relates to what the company expects to put through the system in terms of tons of steel per day or per year etc. This capacity determines the physical size of the mechanical equipment and the line tanks and the mechanical utility requirements.

The chemical capacity relates to what needs to be processed in the chemical system to suit the steel capacity. This capacity determines the size of the chemical equipment, the waste haulage, utility requirements, chemical requirements and the operating procedures.

4.2 Lost and found

Once the steel capacity is known, the chemical capacity can be determined by what the steel-throughput leaves behind in the chemical system or what is "lost" off the steel while pickling.



One way to do this would be to weigh the steel before and after pickling, whereby the difference in weight would be the material "lost" to pickling. The "lost" material of course is millscale and dissolved steel and is normally referred to as IRON LOSS. This weighing process could be quite costly and time consuming; instead, one can use material balance calculations based on operating records. For general purpose discussions, the average iron loss is assumed to be:

0.5 to 0.7% per ton of steel pickled for wire and rod
0.3 to 0.5% per ton of steel pickled for sheet and coils

However, by applying the knowledge gained in the previous chapters and some simple calculations one can determine quite accurately the iron loss in any operation and thus also the size of the chemical equipment, the utility and chemical requirements etc. or how efficiently the system is being operated.

Therefore, the key to the design and operation of the entire chemical system is the IRON LOSS !

4.3 Keeping your Losses to a Minimum

Great effort should be made during operations to try and reduce the iron loss, in order to achieve maximum efficiency or even better than design capacity.

The amount of iron lost depends on:

a) type of scale to be removed.
b) amount of scale to be removed.
c) length of time steel is immersed in acid
d) type of inhibitor used
e) amount of inhibitor used

Since items a) and b) are part and parcel of the type of steel being pickled, no control can be maintained on these two items. However, items c), d) and e) are relative only to plant operations, and can, therefore, be controlled as follows:

c) do not leave steel in pickle bath any longer than is absolutely necessary to remove the scale
d) 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.
e) inhibitor amounts needed are determined by practice and by monitoring the iron loss; too little inhibitor will increase the iron loss, too much inhibitor is a waste (see chapter 6).

4.4 More Ways to Calculate Efficiency

The actual iron loss can be calculated by knowing how much steel had been pickled and how much acid had been used or, if you have a recovery system, how many crystals were produced over a given period of time.

Example: 250 tons of steel were pickled in one day and during that period 7000 lbs. of acid were used and approximately 10 t of crystals were produced.

4.4.1 By Way of Crystals

Crystals are chemically made up as

$FeSO_4.7H_2O$
(56 + 96 + 126 total molecular weight = 278)

i.e. the Fe portion of the crystal is 56/278 = 1/5 of the crystal

Therefore 10 tons of crystals represent 10/5 = 2 tons Fe

This means that the iron loss during that period, based on crystal production for 250 tons of steel was:

2/250 x 100 = 0.8%

4.4.2 By Way of Acid

Since the exact amount of crystals produced is not always possible to obtain, the more accurate way of calculating the iron loss is by using acid consumption figures because this can be accurately determined by tank level change or through purchasing records etc., provided no acid is wasted down the sewer or by trucking it away, in which case, the lost acid must also be considered.

According to the conclusions in chapter 3.5, for every lb of iron dissolved, 1.75 lbs acid is used up.

Therefore, 7000 lbs. acid represent:

7000/1.75 = 4000 lbs. of Fe dissolved

Since the concentration of the acid purchased is 93%, the actual iron dissolved is:

4000 x 93/100 = 3720 lbs.

This means that the iron loss during the day based on acid consumption for 250 tons of steel was:

3720 x 100/2000 x 250 = <u>0.744%</u>

You can see that the results of the two methods differ slightly. That's because the weight of crystals produced was given as "approximate". If the exact weight was known, the two results should match.

4.5 Monitor Your Efficiency

By calculating the iron loss on a regular basis, say once per week, close control can be maintained on the overall efficiency of the plant operation, by making adjustments where necessary. For instance, a sudden increase in iron loss could mean:

- - pickling times too long (over pickling)
- - inhibitor dosage too low
- - acid being wasted (overflowing tanks, leaks, etc.)
- - heavy scale on steel etc.

5.0 ANALYSIS AND CALCULATION METHODS

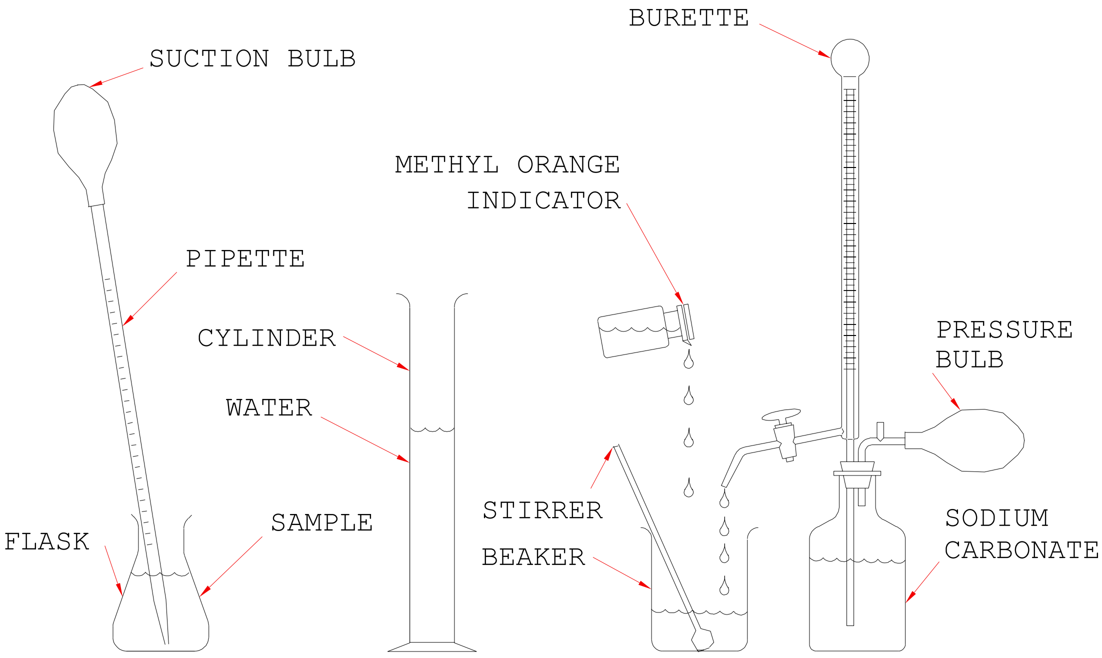
There are various means of analyzing acid and iron content. The methods described below are the ones recommended and have proven most convenient for operating purposes.

5.1 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.

5.1.1 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 = w/v % H_2SO_4.



5.1.2 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.

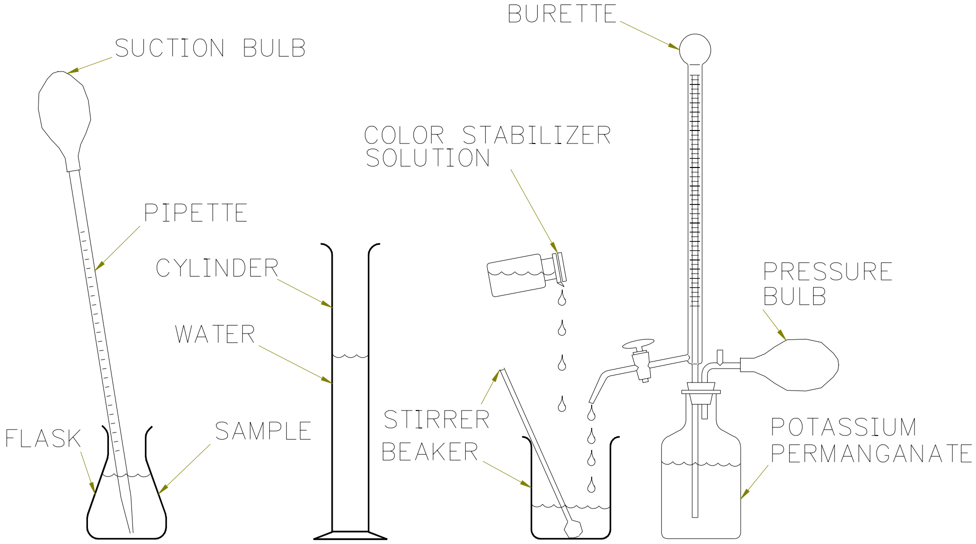
Methyl Orange Indicator Solution
This solution can be purchased ready for use from any laboratory supply company.

5.2 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.

5.2.1 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.



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.

5.2.2 *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).

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.

5.3 Concentration Calculations

5.3.1 *% 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.

5.3.2 *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).

5.3.3 *% 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

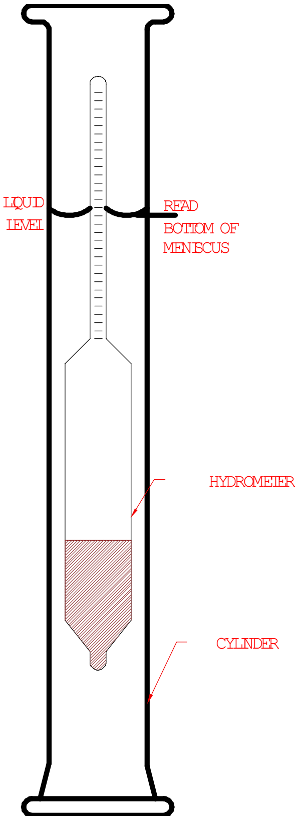
The SG of a solution is the relationship of the weight of that solution to a specific volume, using water as being 1.0. Therefore, if a container holds 10 lbs. of water, that same container would hold 12 lbs. of a solution with an SG of 1.2.

5.3.4 *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.

5.3.5 *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./

5.4 Determination of Acid or Base by pH Method

5.4.1 *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)

5.4.2 *MEASURING pH*

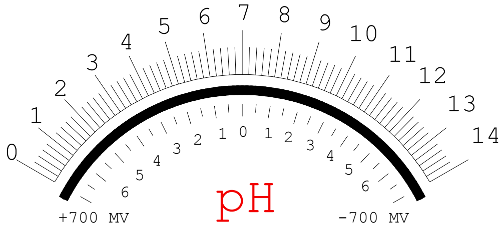
There are two methods available to us to measure pH:

- the pH meter
- pH paper (Litmus paper)

5.4.2.1 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).

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

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

Highly acidic	Red
Neutral	Yellow
Highly basic	Navy Blue

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

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

A final warning about pH measurement: Regardless of what method is used, pH can only be measured in aqueous solutions! i.e. solutions containing water. A solution that does not contain water can be measured only if it is possible to add distilled water for testing.

6.0 USE OF INHIBITORS

As explained in chapter 1, we are depending on acid attack on the steel to get the scale off so why do we need inhibitor?

Because we only want the acid to produce hydrogen under the scale, not on the exposed surface of the steel; otherwise, the steel would be pitted (etched) and rough in spots. We only need very little H_2 to do the job of popping the scale off, so, with a material added that would allow only about 10% of the full force of the acid reaction on exposed steel, yet enough under the scale to do a good job, we would obtain an even smooth finish on the steel and use less acid to boot.

Inhibitors used in proper dosages do exactly that; they provide 90% inhibition. Inhibitors are dispersed in the pickle bath, while acid is dissolved in it. This allows uninhibited acid to creep through the cracks in the scale, to form H_2 and as soon as the gap becomes large enough, the inhibitor gets to work on the newly exposed surface.

Inhibitors will never inhibit better than 90%; therefore, using dosages over and above what is needed, is a waste. On the other hand, they will inhibit less, if dosages are too light, thus wasting acid and producing bad product. This would imply that there is an economical balance somewhere between the acid wastage and inhibitor wastage.

Unfortunately, there is no sure-fire way of exactly determining the dosage requirement, particularly where an acid recovery system is used, because some of the inhibitor is always returned via the recovered acid, and one never knows how much is there.

However, by monitoring the iron loss discussed earlier, a trend in relation to different dosages can be established and thus a fairly equitable 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 pt per acid batch) 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 was 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.

7.0 HEATING THE PICKLE TANKS

7.1 Why heating?

When acid is added to the pickling solution, the solution gains temperature, because heat is evolved, when acid reacts with water ----

When steel is being pickled, the pickling solution gains temperature because heat is evolved, when acid reacts with iron ----

With all this heat being created in the pickling solution, why then do we have to heat the tanks ?

The answer to this is actually quite simple: there is not sufficient heat created by the reactions to hold the tank at a steady temperature because there is a lot more heat than that lost from the system by processing.

The heat being lost from a pickle tank is due to a combination of all of the following:

- Cold steel entering the tank soaks up heat, until the steel temperature is equal to the temperature of the pickling solution
- The tank walls and liquid surface radiate heat, because the atmosphere around them is colder than the pickling solution
- Cold solutions added to the tank soak up heat
- Hot solutions evaporate water to atmosphere which has a cooling effect on the solution, thus creating a loss of heat

Without adding heat to the tanks, the temperature of the pickling solution would be very low, because of these heat losses.

7.2 Making up for losses

Out of all the heat-losses listed, evaporation represents as much as 75% of the total heat loss ! This is the reason for sometimes drastic measures being taken, to curb evaporation from pickle tanks, to conserve heat which translates into energy conservation. Changing the temperature of the pickle tank solution causes drastic evaporation changes:

- twice as much water is evaporated at 180°F than at 160°F
- twice as much water is evaporated at 190°F than at 180°F

Evaporation rate changes exponentially with temperature change. This of course means that the heat input will follow suit so that if you can pickle at 170°F instead of 180°F, you will save a good 50% of the energy needed to do the same job !

The heat loss from the pickle tank can be calculated quite accurately. These calculations will determine the size and specifications of the heating equipment and the fume exhaust system.

7.3 How to Heat

There are several methods available to heat pickle tanks such as:

- electric immersion heaters
- submerged combustion heaters
- steam injection
- steam coils
- steam heat exchangers with circulation pumps

The most common methods used are those employing steam as a heating medium. Better efficiency, lower cost, ease of control and no risk of fire are some of the reasons steam heating is preferred. Because of this, we will concentrate our discussions on steam heating.

7.4 Steam heat, the old standby

7.4.1 Live steam

Steam injection until recently has been the most convenient way to heat pickle tanks, but because of environmental concerns, this method of heating is becoming more and more obsolete as the trend toward effluent free pickling is gaining popularity. When steam is injected into a solution, the resulting condensation of the steam adds slightly more water to the solution than the evaporation of water from the tank. As effluent free pickling depends on evaporating acidic waste waters in the pickle tank, injecting steam in it would not allow waste water to be evaporated.

7.4.2 Steam confined

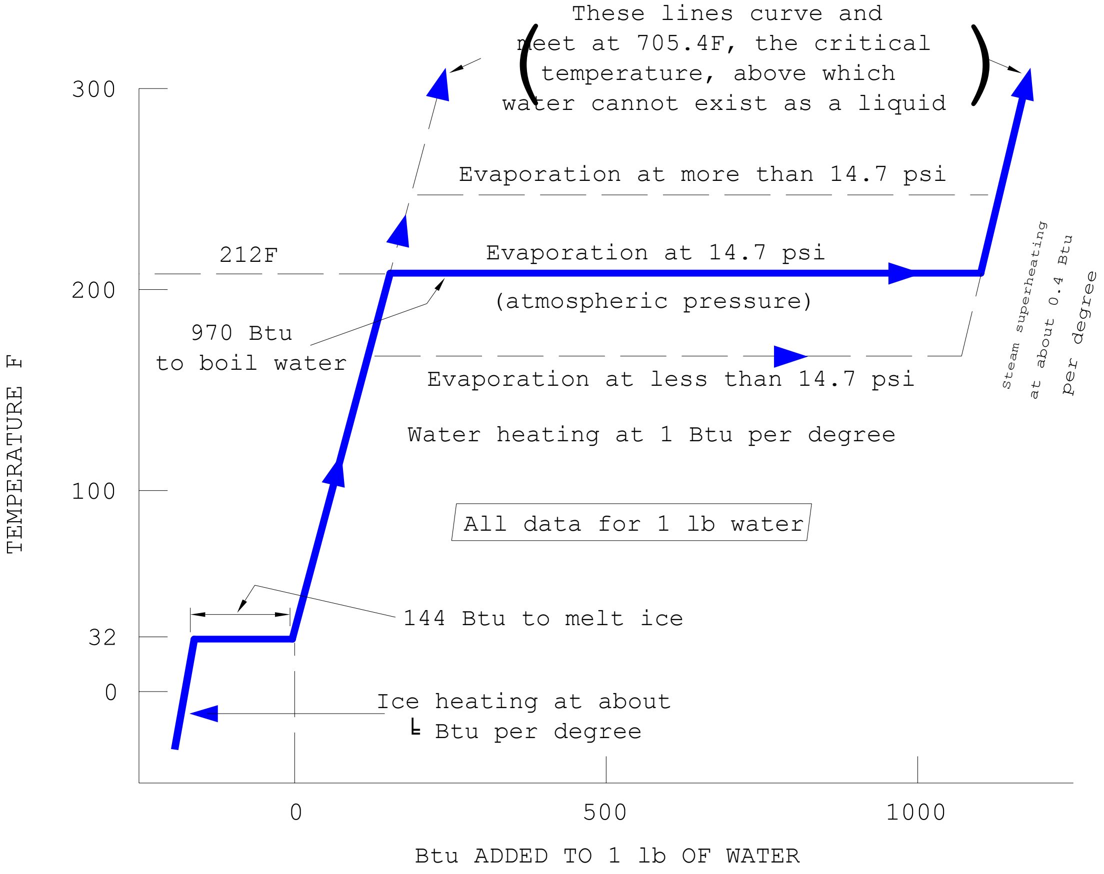
For this reason, non contact or external steam heating is becoming more popular. By using heating coils or external heat exchangers, the steam does not come in contact with the pickling solution; instead the condensate is formed inside the tube or heat exchanger and either returned to the boiler or disposed of as clean water. This way, the solution level in the pickle tank drops steadily due to evaporation, requiring water to be added steadily to maintain the level. What better way to use up rinse water ?!?

7.5 The muscles behind steam

When using external steam heating, it is very helpful to be familiar with some basic facts about steam in general so as to be able to operate the heating system as efficiently and trouble free as possible. To that end, we must accept the following laws of nature:

- matter exists in any one of three physical states: solid, liquid, vapour
- To change any matter from one physical state to another, energy must be added or removed
- energy must be added to change solid to liquid to vapour
- energy must be removed to change vapour to liquid to solid
- heat is a form of energy
- temperature is not a measure of heat
- heat is measured in BRITISH THERMAL UNITS (BTU): the heat input required to raise the temperature of 1 lb of water by 1°F is equal to 1 BTU (e.g. increasing the temperature of 10 lbs water from 100°F to 150°F requires 500 BTU)
- the heat required to change 1 lb of ice at 32°F to 1 lb of water at 32°F is 144 BTU

- -- the heat required to change 1 lb of water at 212°F to 1 lb of steam at 212°F is 970 BTU
- -- when cooling steam to water to ice, the respective heat value is recovered in the medium used for cooling
- -- the temperature of saturated steam increases as its pressure increases



From the above facts, we can conclude, that the energy carried by every lb of steam at atmospheric pressure is worth 970 BTU of heat and that this heat is released when the physical state of the steam is changed to water (condensate, from "condensing" steam).

Steam Tables

PROPERTIES OF SATURATED STEAM

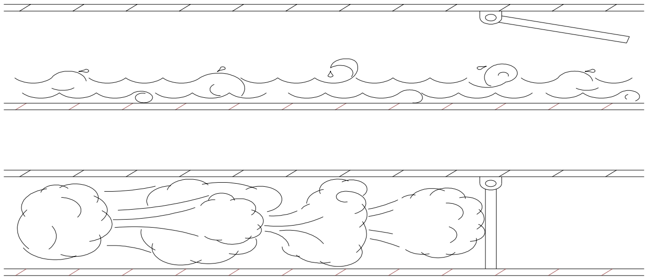
Col. 1 Gage Pressure	Col. 2 Absolute Pressure PSIA	Col. 3 Steam Temp. °F	Col. 4 Heat of Sat. Liquid	Col. 5 Latent Heat	Col. 6 Total Heat of Steam	Col. 7 Specific Volume cu. ft./lb.
29.743	0.08854	32	0.00	1075.8	1075.8	3306
29.515	0.20	53.14	21.21	1063.8	1085.0	1526
27.886	1.0	101.74	69.70	1036.3	1106.0	333.6
19.742	5.0	162.24	130.13	1001.0	1131.1	73.52
9.562	10.0	193.21	161.17	982.1	1143.3	38.42
7.536	11.0	197.75	165.73	979.3	1145.0	35.14
5.490	12.0	201.96	169.96	976.6	1146.6	32.40
3.454	13.0	205.88	173.91	974.2	1148.1	30.06
1.418	14.0	209.56	177.61	971.9	1149.5	28.04
0.00	14.696	212.0	180.07	970.3	1150.4	26.80
1.3	16	216.32	184.42	967.6	1152.0	24.75
2.3	17	219.44	187.56	965.5	1153.1	23.39
5.3	20	227.96	196.16	960.1	1156.3	20.09
10.3	25	240.07	208.42	952.1	1160.6	16.30
15.3	30	250.33	218.82	945.3	1164.1	13.75
20.3	35	259.28	227.91	939.2	1167.1	11.90
25.3	40	267.25	236.03	933.7	1169.7	10.50
30.3	45	274.44	243.36	928.6	1172.0	9.40
40.3	55	287.07	256.30	919.6	1175.9	7.79
50.3	65	297.97	267.50	911.6	1179.1	6.66
60.3	75	307.60	277.43	904.5	1181.9	5.82
70.3	85	316.25	286.39	897.8	1184.2	5.17
80.3	95	324.12	294.56	891.7	1186.2	4.65
90.3	105	331.36	302.10	886.0	1188.1	4.23
100.0	114.7	337.9	308.8	880.0	1188.8	3.88
110.3	125	344.33	315.68	875.4	1191.1	3.59
120.3	135	350.21	321.85	870.6	1192.4	3.33
125.3	140	353.02	324.82	868.2	1193.0	3.22
130.3	145	355.76	327.70	865.8	1193.5	3.11
140.3	155	360.50	333.24	861.3	1194.6	2.92
150.3	165	365.99	338.53	857.1	1195.6	2.75
160.3	175	370.75	343.57	852.8	1196.5	2.60
180.3	195	379.67	353.10	844.9	1198.0	2.34
200.3	215	387.89	361.91	837.4	1199.3	2.13
225.3	240	397.37	372.12	828.5	1200.6	1.92
250.3	265	406.11	381.60	820.1	1201.7	1.74
	300	417.33	393.84	809.0	1202.8	1.54
	400	444.59	424.0	780.5	1204.5	1.16
	450	456.28	437.2	767.4	1204.6	1.03
	500	467.01	449.4	755.0	1204.4	0.93
	600	486.21	471.6	731.6	1203.2	0.77
	900	531.98	526.6	668.8	1195.4	0.50
	1200	567.22	571.7	611.7	1183.4	0.36
	1500	596.23	611.6	556.3	1167.9	0.28
	1700	613.15	636.3	519.6	1155.9	0.24
	2000	635.82	671.7	463.4	1135.1	0.19
	2500	668.13	730.6	360.5	1091.1	0.13
	2700	679.55	756.2	312.1	1068.3	0.11
	3206.2	705.40	902.7	0.0	902.7	0.05

PSIG Inches of Vacuum

7.6 Lets get practical

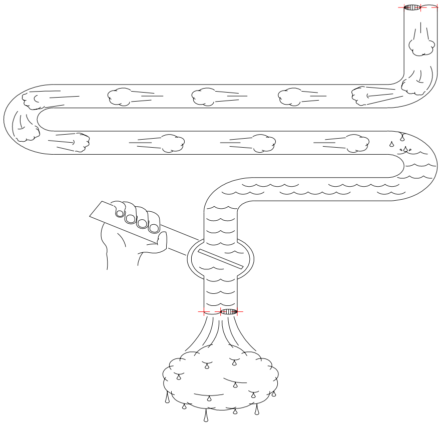
7.6.1 Condensate, a hot issue

In practice, this means, that the steam must be converted to condensate in close proximity of the pickling solution (i.e. heating coil or heat exchanger) for it to gain the heat carried by the steam. For this to take place, the steam must be held within the heat transfer equipment until it is converted to condensate, then the condensate must be drained away, to make room for more steam to be converted.



7.6.2 A trap of a different sort

One way to accomplish this would be to install a valve on the condensate exit of the equipment and stand there opening and closing it as required to let the condensate pass. Or, one could adjust the valve opening just enough to allow the condensate to flow through continuously but not the steam. Fortunately a device has been invented to do just that without having to stand there, it is called a STEAM TRAP.



There are many types and makes of steam traps on the market, all doing the same job but made for specific applications. Which traps to use where is best left up to the trap manufacturers, and most of them have excellent literature available to learn more about steam usage, steam piping, condensate piping, and steam trapping.

7.6.3 Temperature under control

Having installed a trap on the condensate outlet of the equipment is perhaps the most important step taken in assuring proper heating of the pickling solution. There still remains the steam supply to be controlled, because if left just to the trap, you will find the temperature of the pickling solution increasing steadily, as steam is continuously converted to condensate. Theoretically this temperature rise could continue until the temperature of the pickling solution equalled the temperature of the steam.

Because the temperature changes in the pickling solution are a good indication of heat requirement, and the heat load is dependent on lbs of steam needed (or lbs of condensate produced), it stands to reason, that in order to maintain a steady solution temperature, we need to control the FLOW of the steam. Again, we can install a valve but this time on the steam input to the equipment and again we can stand there and adjust the valve but this time according to the temperature of the solution: opening when the temperature drops and closing when the temperature increases. The gadget invented to do this for us is a TEMPERATURE CONTROL VALVE.

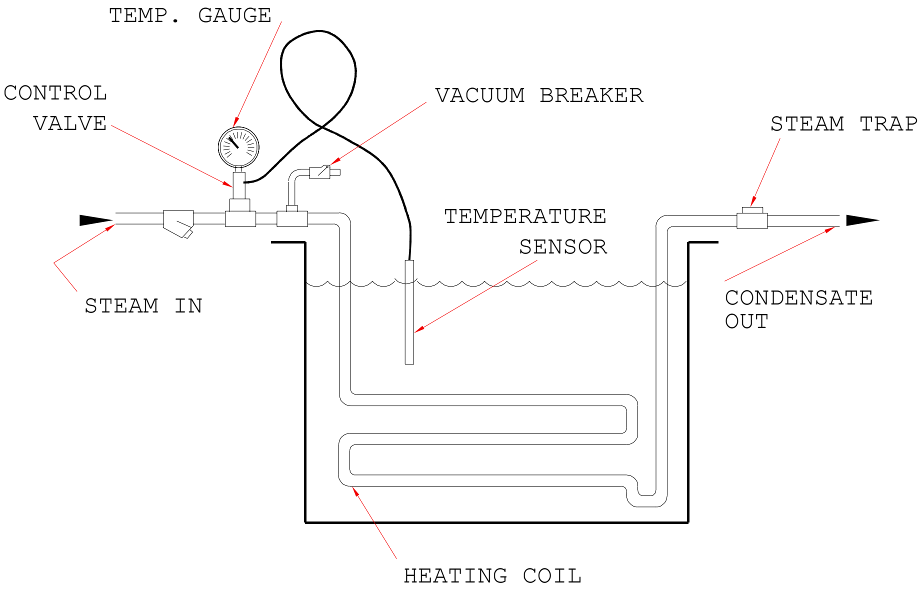
The most commonly used valves for this purpose are direct acting capillary types. These valves are operated by the pressure changes within a liquid filled capillary. When the capillary is immersed in the pickling solution, the liquid in the capillary expands and contracts proportionally with the temperature changes in the pickling solution. This varies the pressure within the capillary which is attached to a cylinder with a spring loaded piston operating the valve stem. Other steam control devices are used, such as proportional controllers, both pneumatic and electronic.

7.7 Dangerous Vacuum

When it is necessary to inject live steam directly into the pickling solution and the main stop valve is shut, any steam left in the supply pipes will condense and for a short time a partial vacuum will form as the volume of the condensate is much less than that of the steam. As a result, liquid will be drawn into the piping and may reach the steam control valve. which is susceptible to corrosion.

A similar problem can occur where pickling solution is heated by means of steam pipe coils fitted with steam traps. When steam is turned off, a partial vacuum will form in the coil and any slight leak in the latter will allow corrosive liquid to be drawn into the system. Again, corrosion damage is likely to occur.

The simplest way of preventing the formation of this vacuum is to fit a check valve in reverse to a branch in the steam supply line. Fitted in this way, the check valve will be closed when steam pressure is present, preventing any loss of steam. When the supply valve is closed and the steam left in the system condenses, atmospheric pressure will open the check valve and prevent the formation of a vacuum by allowing air to enter the heat exchanger.

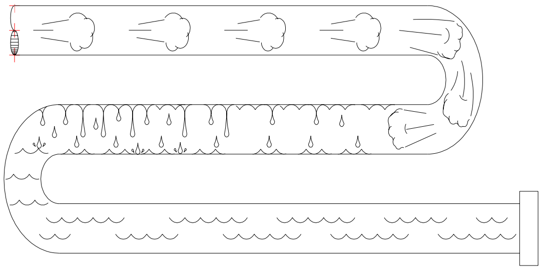


7.8 Keep it perking and save energy

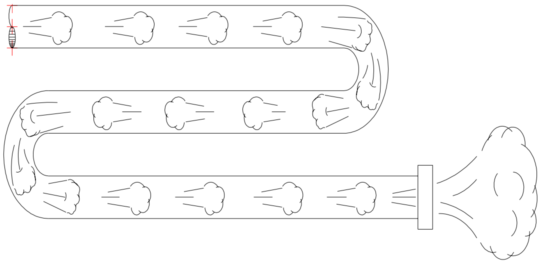
Having the temperature in the pickle tank more or less under control, there are some items of interest needing explanation in terms of maintaining the steam heating system.

As discussed before, the trap is probably the most important device in the steam heating system. It is therefore very important that it be properly maintained and kept in perfect operating condition. Knowing that heat transfer depends entirely on converting steam to condensate, it can be deduced that if the trap is either stuck shut or stuck open, heat transfer is virtually non existent for the following reasons:

- - TRAP STUCK SHUT: condensate will not pass, the heating equipment will fill with condensate, the temperature will drop, the control valve will open wide, but no steam will flow and heating stops.



- - TRAP STUCK OPEN: steam is not retained in the equipment long enough to form condensate, steam blows right through the trap, the temperature will drop, the control valve will open wide, the heat carried by the steam is released after it leaves the trap and heating stops.



Please also remember, that energy wastage can be enormous if the heating system is not in proper working order. It is therefore advisable to institute a preventive maintenance program which at regular intervals provides for the following:

- - cleaning of strainers
- - checking of trap operation
- - check of control valve operation
- - check of vacuum breakers

This is just as important as regular greasing of mechanical equipment to prevent unexpected production interruptions.

8.0 RINSING

8.1 Why Rinsing?

Rinsing is a necessary evil in the pickling process. Without rinsing, pickling would be more or less useless as residual acid on the steel would cause more corrosion and formation of oxides on the steel surface, which would again need removal before further processing.

Rinsing has one purpose only and that is to wash off any residual pickling solution left on the steel. If you want to remove scale, grease, soot, lime or whatever from the steel don't look to the rinse tank to do it!

8.1.1 It's A Drag

When the steel leaves the pickle tank, there is a film of pickling solution (acid and iron sulfate) left on the surface of the steel. This film is there even though the majority of the "liquid" pickling solution has drained off while the steel is being removed from the pickle tank. The film on the steel is then "dragged" out of the pickle tank into the rinse tank, thus the amount of liquid in the film is referred to as **drag out**. The purpose of the rinse section therefore is to wash off the drag out film from the steel surface and replace it with clean water.

8.2 The Niagara Falls Syndrome

Until recently it was quite common to remove this film by literally inundating the steel with enormous quantities of water under unbelievable pressure. This of course did a wonderful job because the same effect could be achieved by running the steel under the Niagara Falls (American or Canadian, either would do).

But then who would want to pay that water bill or worse the bill for treating all that rinse water. For this reason, methods had to be devised to provide satisfactory rinsing with less water consumption which also reduces waste water production.

8.3 The Theory

To achieve these reductions, we have to look to the technology which applies to rinsing. Theoretically, all that needs to be done is to replace a film of unwanted liquid with a film of wanted liquid; this means that for every gallon of pickling solution on the steel, a gallon of water is needed to replace it. On an average, the drag out (**if the steel is properly drained**) amounts to approximately 10% of the iron loss in terms of dissolved iron in the film. Thus we can calculate as follows:

- - If iron loss, for example, is 0.7% then 1000 lbs of steel produces 7 lbs of iron in solution
- - If the pickling solution contains say
  6% w/v iron = 60 g/1000 ml = 0.13 lb/0.26 gal
- - Therefore the iron loss equivalent is 7/0.13 x 0.26 = 14. gal.
- - 10% of that is 1.4 gal/1000 lbs of steel drag out or 2.8 gal/ton

According to the above theoretical analysis this means that 2.8 gal of water should be needed per ton of steel to replace the drag out. This is a far cry from Niagara Falls! and you are just now saying: "impossible".

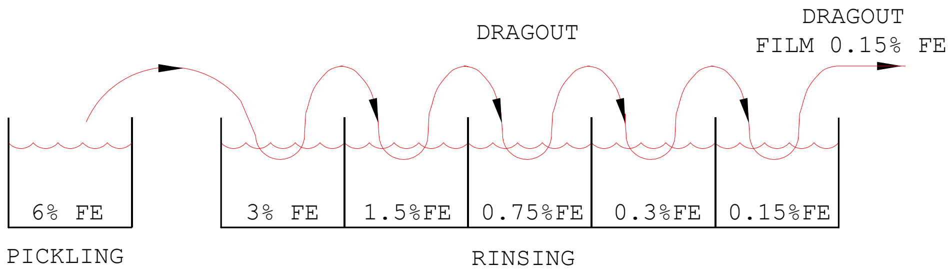
8.4 Beating Impossible Odds

Lets look at the impossibility of the previous discussion by convincing ourselves that we do not have any other choice and that we simply have to only use 2.8 gal per ton or we have to give up pickling all together. With this positive goal in mind, we can now start devising a system which will make the impossible possible.

8.4.1 Dilution, What a Solution!

Let us consider that if we could dilute the film on the surface of the steel, before we actually apply the clean water, then when the clean water is applied, the concentration of iron sulfate and acid in the film would be much less and therefore would wash off more easily and better yet, let us assume that we can dilute the diluted film even more, and more and more; then finally we would end up washing off a film which would almost be clean water! OK, but where is all that dilution water coming from? Obviously we can't add it to the system or the whole purpose would be defeated. So now what?

How about running the steel through a series of tanks each containing progressively more diluted picking solutions:



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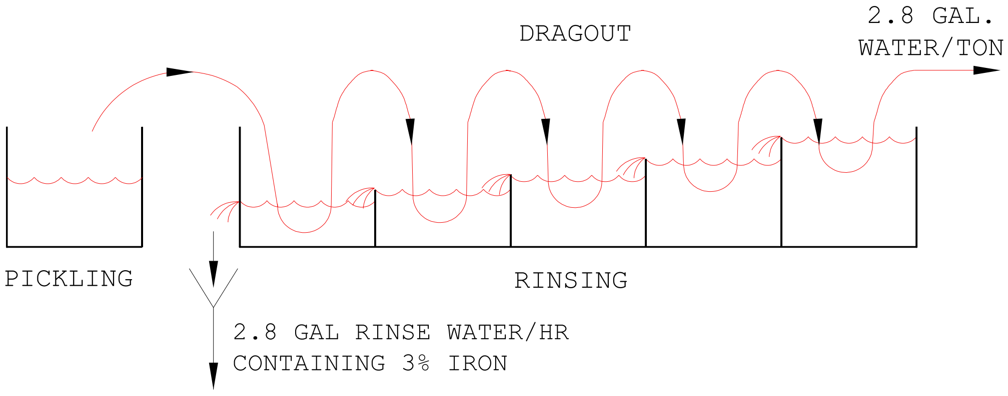
8.4.2 A Water Fall of a Different Nature

The result would be that the steel would leave the rinse section with a very dilute film of pickling solution. Now how to keep these diluted solutions that dilute? How about adding our 2.8 gal of water per ton to the last tank in the system and making it overflow to the next one and the next and the next etc. until it runs out of the first tank sort of like a cascading waterfall.



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8.4.3 The Final Rinse

Now we still have the steel leaving with a film of dilute solution. To get rid of that, we simply make the fresh water go over the steel leaving the last rinse tank before it falls into the tank. Because the iron content in this last film is so low compared to what our initial calculation was based on, the 2.8 gal/ton is actually about 5 times more than what would be needed to do the theoretical rinsing at that point, thus assuring good rinse and good dilution through what now has become a **cascade rinse system** or counter current rinse system or multi-stage rinse system.

8.5 Let's Get Practical

All of the above discussion makes you think: fine and dandy but how does this apply to my pickling in my plant in my part of the woods? Perhaps we should define rinsing into two major applications:

- rinsing for continuous pickling
- rinsing for batch pickling

8.5.1 Rinsing for Continuous Pickling

In most systems of this type, cascade rinsing is already a household word; however, we find in a lot of cases that even though the equipment for cascade low volume rinsing is in place, the Niagara Falls syndrome still is alive and well. In other words, all kinds of effort and excuses are generated to not make the system work properly.

There is no one single reason for this; a lot of factors come into play such as:

- waste water treatment is cheap
- water costs are low
- nobody gives a damn
- nobody knows how it's supposed to work
- too much trouble to operate
- too much trouble to maintain
- we worked well without it for 30 years
- it stains the steel
- the nozzles always plug up, so we put a fire hose in it
- etc. etc.

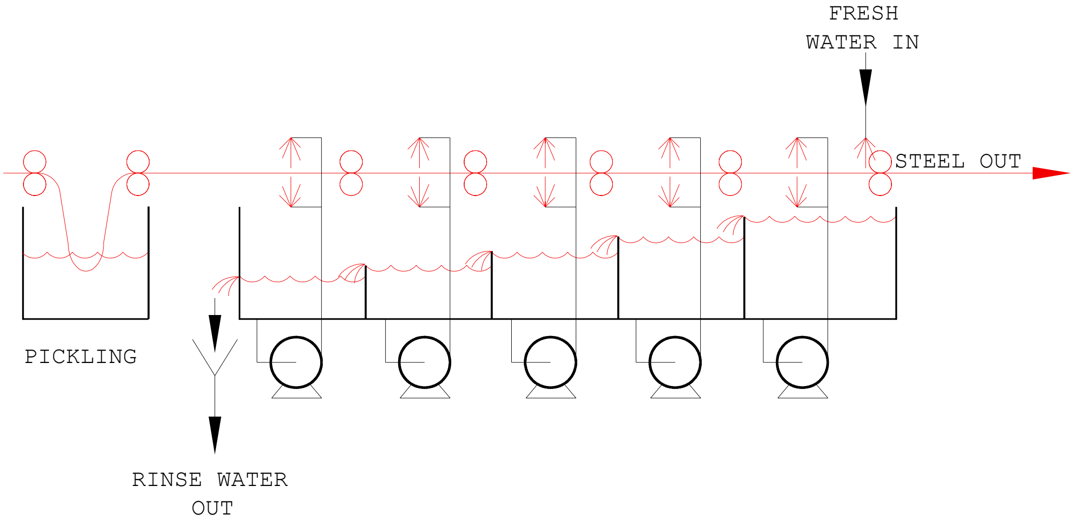
All of the above only point to one major problem to be confronted: there is **no incentive** to make it work right. As long as the extra costs involved in running Niagara Falls through the rinse section are ignored, then why bother.

Therefore if you do have a cascade rinse system which is not or does not want to be operated properly you are literally wasting hundreds of thousands of dollars per year and it would be in yours and everyone else's interest to find out why it is not used properly and then to get it working.

Remember, it was designed with sound economical and technological principles in mind and if there are any shortcomings in its design, the economical benefits in getting it right would outweigh the costs for modification.

There are plenty of experienced engineering firms available to study your system without bias and make suggestions as to how to make the system workable.

Basically, the cascade rinse system in a continuous pickle line, be it strip, rod or wire, works almost exactly as described in 8.4.2 and 8.4.3 above with two exceptions: instead of the steel dipping through the tanks, it passes straight through and the solution in each tank is circulated by pumps and sprayed onto and under the steel



The drippage between stages is accomplished by having the steel pass through squeegee rolls or wipers which will return all but the film on the steel to the tank it came from.

8.5.2 Rinsing for Batch Pickling

Presently most batch pickling operations are or have been in the process of eliminating the Niagara Falls syndrome for environmental and economical reasons. There are many ways to apply the technology discussed and many picklers are trying hard to arrive at some sort of two or three stage system suitable for their particular operation.

In most "home made" applications however, we find that the system was abandoned because it was not meeting certain preconceived expectations. Even in the case of some of the properly engineered systems, we find this to be the case.

When this happens, we can usually find that although the system on paper looked very promising, certain pre-requisites to making it work were ignored. To change from Niagara Falls to multi-stage, low volume rinsing regardless of how good or how expensive the system being installed is, the following must be considered:

- extra time for dripping above the pickle tanks must be allowed **before** entering the rinse tank
- you must accept the fact that the 1st stage rinse will be very dirty and high in acidity
- you must allow ample time for the power rinse to run
- you must allow ample time for drippage between rinse stages
- you must allow ample time for the final clean water rinse to penetrate the rod coils
- the logistics of moving the steel through the pickle line must be changed to suit the new rinse system
- you must never rinse anything but pickling solution in the rinse tank
- the rod coils must be suspended loose, not bound
- the engineer designing your system must know your feelings about all of the above besides the total tonnage expected as it affects the size and cost of the equipment

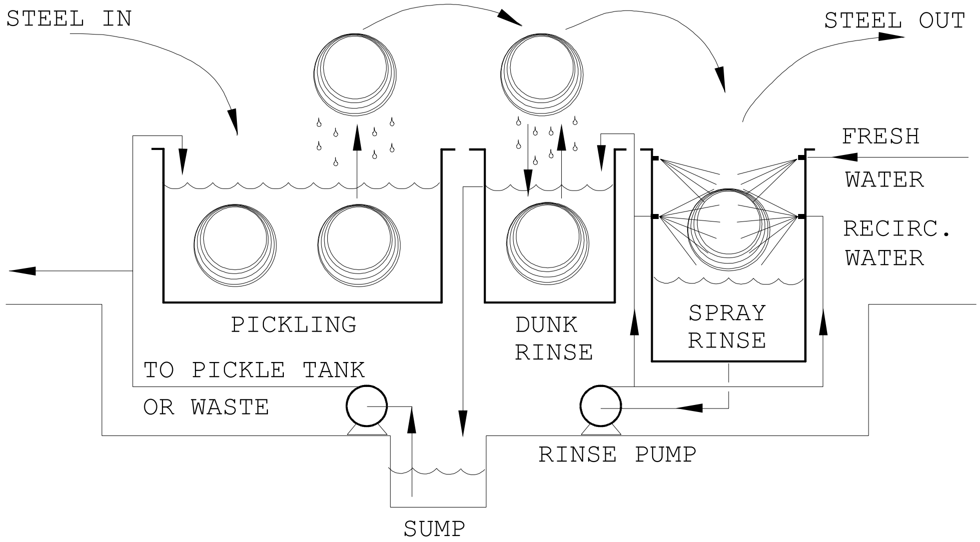
All of the above must be outweighed by the economical benefits due to:

- reduction in water consumption
- reduction in rinse water treatment cost (operating and capital)
- reduction in rinse waste haulage
- possible elimination of rinse waste treatment and rinse waste haulage
- possible recovery of some acid

before the decision is made whether or not to go to multi stage rinsing.

Once you do, or if you already have a multi-stage rinse system, its operation is similar to that outlined in 8.4.2 and 8.4.3 with the exception that there are only two or three stages and there may be a combination of dip/spray rinse. The basic principle is the same: each stage works on a slightly more dilute solution than the one before and the final rinse is applied directly to the steel.

It is actually possible (space permitting) to have a three stage rinse system in your pickle line.



Two rinse tanks will be required, the first one being a simple dunk rinse. Here the majority of the acid trapped in the rod coils will be replaced with the dilute rinse solution from the 2nd stage. After adequate dripping on removal of the steel from this tank, it is suspended in the spray rinse tank where the remaining dilute film on the steel is replaced by a more dilute power spray from the reservoir in the bottom of the spray rinse tank. After adequate spray and drip time, the final 3rd stage fresh water spray which is a fine low volume mist will replace the very dilute rinse solution from the 2nd stage.

All of the above sequences can be automatically timed to include the important drippage times between stages.

Note that you have the option to either overflow the rinse water to a treatment or haulage system or eliminate the waste completely be returning the rinse water to the pickle tanks where it will be evaporated. Because of the low water volume required for rinsing, it is therefore possible to actually operate a pickle line effluent free.

Here again, plenty of excuses will be found to revert back to Niagara Falls. But you must consider that any inconvenience created by the multi-stage rinse system is outweighed multi-fold by economical and environmental advantages.

Try it, you'll like it!

9.0 **Fume Extraction**

9.1 Why Do We Need It?

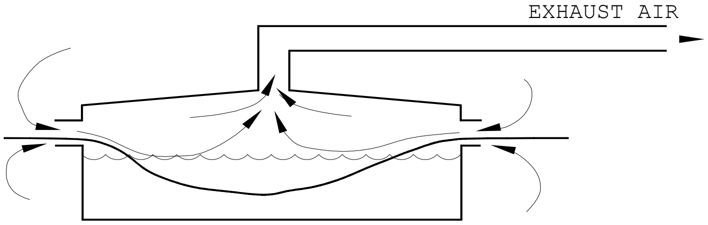
Regardless of the type of pickling facility or the method of tank heating, there is evaporation from the pickle tanks. Though this is desirable for pollution-free pickling, in that it consumes rinse water, it is a nuisance to the people working there and creates havoc with equipment. It is, therefore, necessary to remove the vapours created by evaporation from the immediate area and exhaust them to atmosphere. Unfortunately, these vapours are not just water vapours; they contain minute amounts of acid, which cannot simply be exhausted to atmosphere and filters or scrubbers are required to make this exhaust safe for the environment.

There are two basic methods of exhausting vapours:

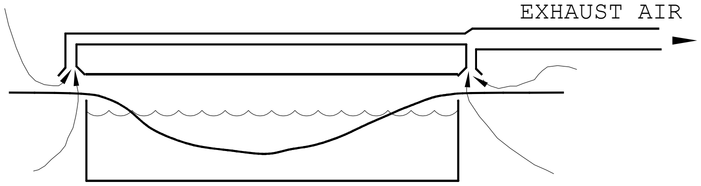
closed tank exhaust
open tank exhaust

9.2 Exhausting Closed Tanks

On closed pickle tanks, such as on strip picklers, the tank covers usually form the hoods. These hoods are connected with exhaust manifolds and are kept under negative pressure by an exhaust fan. The air drawn through the system enters the hoods wherever there are openings, i.e. at the squeegee rolls, where pipes enter, where the steel enters and leaves etc. By this method, the air entering the openings is drawn over the top of the acid toward the hood duct, thus creating high air flows across the acid, which increases evaporation and, therefore, heat input. It can also create excessive entrainment of acid into the air-stream due to high velocity in the confined space above the acid.

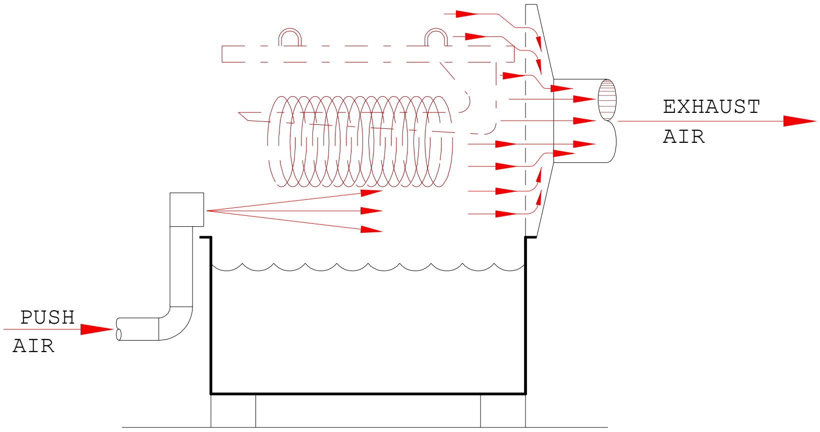


Another method is to extract the vapours where there are openings, thus reducing the air flow across the acid and, therefore, reducing the heat requirement.



9.3 Exhausting Open Tanks

Fume extraction from open tanks requires that the rising vapours are directed to an extraction hood to one side of the tank. This is accomplished by directing a flow of air across the tank toward the hood. This is called push air or air curtain. Because steel is lifted out of these tanks, the exhaust hoods are usually quite high to extract as much of the vapours as possible rising from the hoisted steel. These hoods are fitted with horizontal slots of various widths, they are not just open and they are sized to ensure proper distribution of air flow over the whole height of the hood. These slots can be blocked here and there, to suit air flow requirements; the areas which need blocking are easily determined by observing the vapour flows.



The push air is supplied by a separate push blower. The air from it is directed to the air curtain pipes or ducts which are mounted in or just below the top of the front of the pickle tanks. The air is released from these ducts or pipes through exactly sized holes or slots pointing horizontally across the tank. These openings are designed to carry the exact amount of air required to suit the particular application and applicable safety codes, and they should, therefore, be kept clean and not tampered with and the air intake screen on the push air blower must be kept unrestricted at all times.

The air and vapours collected in the exhaust hood are ducted to an exhaust fan which discharges into a filter or scrubber and hence to atmosphere.

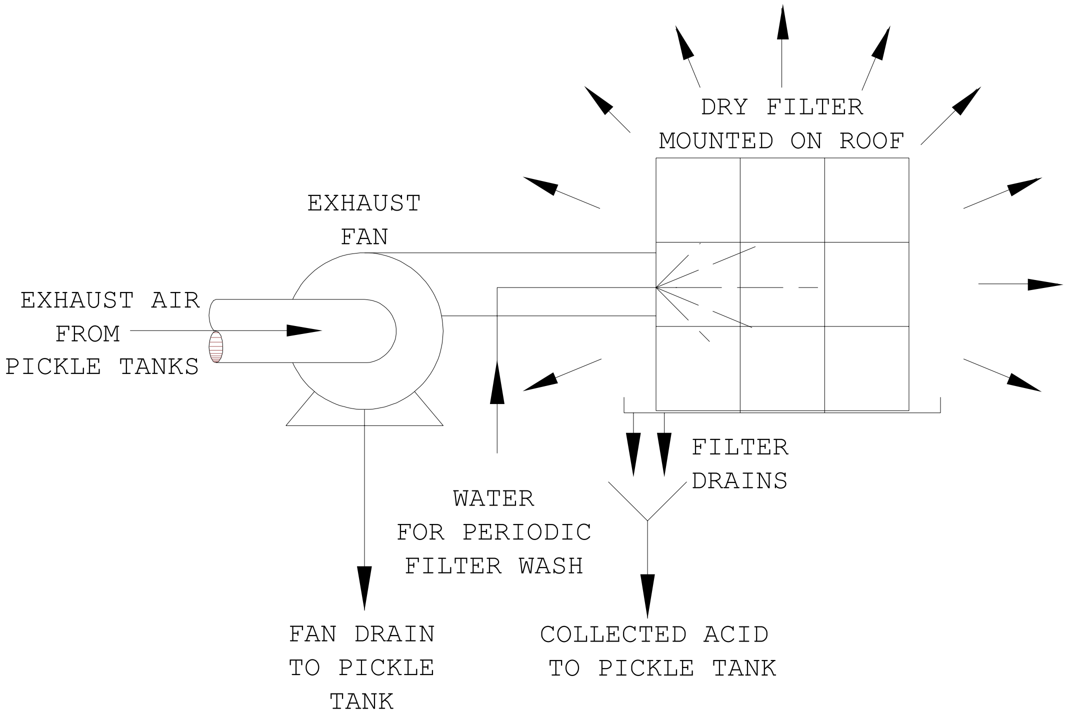
9.4 Save the Environment

The vapours being drawn off any sulfuric acid pickling system are composed of approximately 99% water vapour, with 1% being a mixture of hydrogen and microscopic sulfuric acid droplets. At normal pickling temperatures, sulfuric acid does not evaporate and is odourless. However, there is a certain amount of liquid acid entrainment in the water vapour and the usual "pickle house" smell originates not from the acid but rather from hydrocarbons being released with the hydrogen as the steel dissolves.

This mixture of materials is mixed with the air drawn through the hoods and eventually enters the filters or scrubbers before leaving to atmosphere.

9.4.1 Dry Filtering

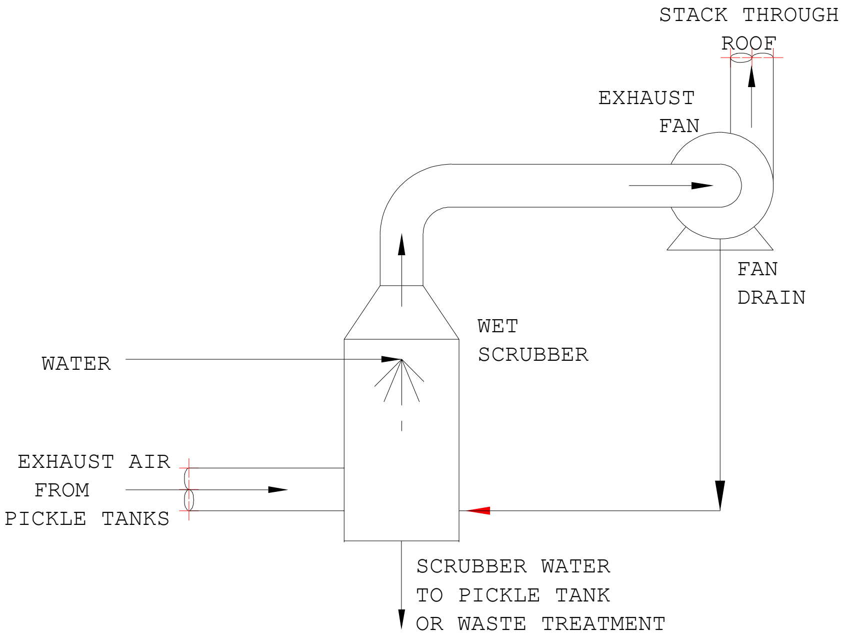
The vapour filter removes entrained acid droplets (acid mist) by allowing them to grow large enough so that their weight overcomes the velocity of the air flow, and they run down along the filter fibres into a collection pan, together with small amounts of condensed water vapours. The collected acid is then returned by gravity to the pickle tanks.



This method of vapour filtering is based on the fact that liquid droplets separate when exposed to change of direction of flow and reduction in velocity.

9.4.2 Wet Scrubbing

On some other exhaust systems, wet scrubbers are used to scrub out the entrained acid. This is accomplished by having the exhaust mixture contacted by a continuous stream of water, so that the acid mist is absorbed by the water. There are various types of wet scrubbers on the market. Some use a lot of water, thus creating another pollution problem; others are designed to use very little water; so little that it can be returned to the pickle tanks and evaporated again.



NOTE: SCRUBBER INSTALLATION IS AHEAD OF FAN TO PREVENT UNSCRUBBED AIR ESCAPING INTO THE PLANT THROUGH POSSIBLE LEAKS.

9.5 Cake in Your Ducts

It is important to note that there is also a very fine mist of ferrous sulfate entrained in the exhaust air. This material usually collects on the inside of the ducting, the fan housing and the fan blades, the filter material and the walls of the scrubber. As it collects there, the water slowly evaporates from it leaving a high concentration of ferrous sulfate and acid, which forms mono hydrate. This material sticks to the surfaces as a white cake and continues building up to the point where fans go out of balance and louvers will not move etc. The only way to prevent these problems is to thoroughly moisten and wash the inside of the exhaust system **daily** to prevent the formation of monohydrate - once it forms, it will not wash off.

9.6 Breathe Clean Air

Exhaust systems do not contribute to the making of profit in your plant; they are a costly capital expenditure with no chance for payback. For this reason, they are sometimes grossly neglected. However, safety codes and environmental controls require that exhaust systems are used and must be engineered to meet certain standards. By keeping the system in good operating order, you will contribute to healthier atmosphere within the plant, a safe environment and a saving in maintenance expenses, which cannot be evaluated in financial terms but which improves productivity and profitability.

10.0 Processing With Acid Recovery

10.1 Prerequisites

To fully understand this chapter, you must be familiar with chapters 1, 2 and 3. We will discuss a generic type of batch process, which will consist of the most common basic pieces of equipment. Alternatives will be discussed at appropriate times, regarding operation and equipment.

The intent here is not to give you a crash course in pickling and acid recovery but rather an insight into the practical application of the theories discussed previously.

10.2 The Flow Diagram

Any chemical process can not be described properly unless you have a flow diagram to follow. The flow diagram to the process operation is like a schematic to the electrician: every piece of equipment and every device is shown on this diagram so that the operator can trace the material flows and find the devices which control the system.

A flow diagram has the equipment arranged in a way to suit the diagram, not the actual plant layout except for the vertical relationship between equipment and floors, so that the operator can "see" where there is gravity flow or pumped flow.

On an engineering flow diagram, each symbol used represents a type of device or equipment. On a simplified flow diagram such as is presented here, the symbols indicate generic devices and equipment. For instance, the symbol for a valve does not indicate whether it is a ball, globe, diaphragm etc. valve, it simply indicates that there is a means to adjust or stop the flow.

Instruments are simply shown as circles and the abbreviations inside the circle indicate what variable the instrument is working on. For instance: PI = pressure indicator, FC = flow controller, TIC = temperature indicator controller etc. etc. If an instrument is controlling a process variable, then the circle is on the line where the variable is measured and a dashed line from the circle to a control device indicates which device it controls.

Other than this, it is a matter of following the line (piping) to find out what goes where and how and to get an impression as to how it is supposed to work.

10.3 The Process Description

Together with a simplified flow diagram is a process description, which describes in general terms as to what is supposed to happen, where and when. The following describes the process as portrayed in the flow diagram on page 53.

10.3.1 Pickling

Note that the pickling and rinse section are not shown on this diagram because the pickling process is rather self explanatory. However, it is important to note that water make up and acid batch make up are part and parcel of the recovery process and will be referred to during the following description.

10.3.2 Batch Acid Recovery

Spent acid containing as much iron as possible is pumped from a spent pickle tank to the spent acid tank. This tank is kept warm so as not to crystallize the iron sulfate. The spent acid solution is pumped by the spent acid pump to the crystallizer where the solution is continuously agitated. At this point concentrated sulfuric acid is added to bring the solution in the crystallizer to the acid concentration desired when it is returned to the pickle tank.

The cooling coils inside the crystallizer contain a brine or glycol solution which is circulated through a chiller system (refrigeration) which keeps this solution at temperature lower than that of the spent acid in the crystallizer. This causes the spent acid to cool and eventually ferrous sulfate heptahydrate crystals will form.

NOTE: some systems do not use an intermediate cooling medium; instead the refrigerant from the chiller unit is circulated directly through the cooling coils or heat exchangers in contact with the acid.

At this stage, control valve CV1 at the bottom of the crystallizer will open and the crystal pump will start circulating the crystal slurry to the settler, where the crystals will separate from the solution and the solution returns to the crystallizer. This circulation is maintained until the solution in the crystalliser reaches its minimum possible temperature, at which time all the crystals will have been produced and are settled in the settler.

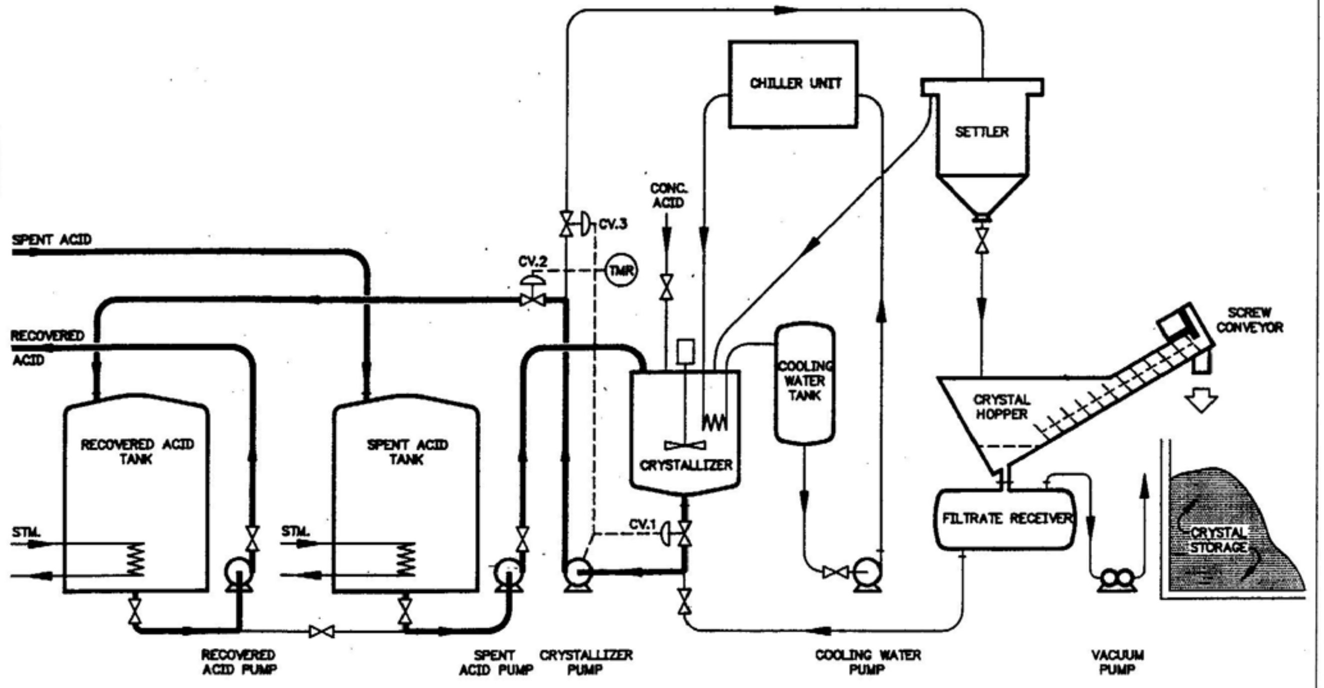
NOTE: some systems employ multi-stage crystallizers without settlers.

Circulation to the settler at this stage is stopped by opening CV2 which allows the crystal-free solution in the crystallizer to be pumped to the recovered acid tank. When the crystallizer is empty, the crystal pump stops and CV1 and CV2 close. The recovered acid in the recovered acid tank is re-heated and is waiting to be used for recharging of a pickle tank to be emptied into the spent acid tank.

When re-filling the pickle tank, it is important to add the water lost during crystallization. This water should come from the rinse tank, thus recovering the acid in the rinse tank. Fresh water is then made up to the rinse tank if necessary.

The crystals are now resting as a thick slurry in the settler. This slurry is dropped into the crystal hopper which also doubles as a "filter funnel". The slurry will fall on a filter screen which allows the solution to fall through to the filtrate receiver, but holds the crystals back. A vacuum pump is started to create an air flow through the bed of crystals above the screen so as to drain any trapped solution through the crystal bed. During this stage, the crystals can be rinsed with water but this is not always necessary.

The dried crystals are then transported by built in screw conveyor from above the screen to a stock pile or into transport containers. The filtrate is pumped via crystal pump back up into the settler to await the next batch of crystal slurry.



ACID RECOVERY SYSTEM

SIMPLIFIED FLOW DIAGRAM

WHS

NOTE: some systems employ centrifuges instead of filter hoppers which also eliminates the vacuum pump and the screw conveyor.

The above described cycle is repeated as dictated by the solution in the pickle tanks "becoming of age".

10.3.3 Continuous Acid Recovery

The above process can be converted to continuous processing by addition of more instrumentation and controls. In this case, instead of pumping batches from vessel to vessel all the equipment would run continuously. The pickling solution would be continuously pumped through the spent acid tank through the crystallizer, through the settler, through the recovered acid tank and back to the pickle tank. Water and acid would be made up automatically in the circulating system not in the pickle tank. Crystals would be continuously removed from the settler and so on.

The engineering, equipment type and size would need to be adapted to continuous processing. In other words, the process described above would need some re-design.

The continuous recovery processes on the market today vary from multi-stage crystallizers cooled by either brines or refrigerant to use of centrifuges, continuous filtration etc. Whatever system is being used or is intended to be used in your plant, they pretty well follow the same basic principles described above. Some are more complicated than others; some are more efficient than others; some are even better to look at than others; whatever the case may be, they all need to be operated properly by people with enough background knowledge to understand what makes them tick.

10.3.4 Remember That:

- Not all the acid used in pickling is recovered - only the free acid (unused acid) in the spent acid is recovered
- A fair amount of water is taken out of the spent acid to form the crystals
- To make up a new batch of pickling acid using recovered acid you must replace the water that was removed with the crystals
- Monohydrate is formed in the pickle tank if you go too high on iron and/or acid and the monohydrate will **stay** in the pickle tank.
- Adding acid to the crystallizer rather than the pickle tank will improve crystallization
- You save time if the recovered acid is re-heated before it is re-used.
- Crystals can form anywhere where there is spent acid that's allowed to cool; therefore flush out stagnant spent acid piping
- To process effluent free you must use water sparingly; it all needs to be evaporated from the pickle tanks or removed with the crystals

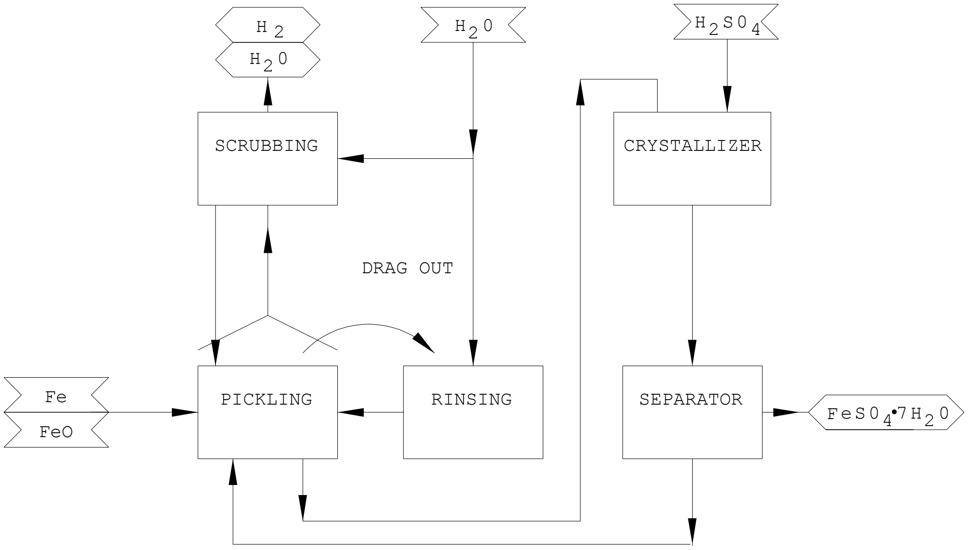
11.0 Balancing the Process

We now realize that pickling and acid recovery are chemical processes and as such can and should be logically explained. There is no room for chance or "magic" happenings. Basic physical and chemical principles apply to all phases of the process. As Newton explains: for every action there must be an equal reaction or there exists an imbalance. Translated into chemical processing, this simply means: what goes in must come out; or, the total amount of material entering a process must equal the total amount of material leaving the process, regardless of any physical or chemical changes that have taken place.

In a pickling and acid recovery process are four separate materials that enter the system and therefore must be removed.

Acid	(H_2SO_4)
Iron	(Fe)
Iron Oxide	(FeO) (any form)
Water	(H_2O)

The first three combine to form ferrous sulfate ($FeSO_4$), hydrogen (H_2) and water (H_2O). The $FeSO_4$ is removed as crystals ($FeSO_4.7H_2O$) and H_2 leaves as a gas and the H_2O is added to the remainder of the solvent water in the system. Because there is a permanent inventory of solution in the system, it therefore stands to reason that if more or less $FeSO_4$ is removed, its concentration in the solution inventory will rise or fall respectively.



EFFLUENT FREE PICKLING

WHAT GOES IN MUST COME OUT AND BE BALANCED

FeO + Fe + H_2O + H_2SO_4 MUST EQUAL H_2O + $FeSO_4 \bullet 7H_2O$ + H_2

The water added to the system has three chances to be removed:

- \- overflowing to sewer
- \- evaporation
- \- chemically combined with crystals

Because overflowing means that also acid and ferrous sulfate are leaving via sewer, it cannot be allowed in a pollution free system.

Evaporation of water takes place at all times, but is limited by the operating conditions at hand.

The water leaving by chemical combination with the crystals is limited to the crystal production.

This means that the maximum amount of water that can be removed from the system is equal to the sum of the amounts removed by evaporation and crystal-removal.

If more than this amount of water is added, the volume of inventory will increase and if not curtailed, solution has to be removed in some way. On the other hand, if there is less added, the volume of inventory will decrease which, of course, is easily remedied, by adding more water.

The water leaving by evaporation can usually be balanced by adding rinse water on a continuous basis to the pickle tanks to maintain the tanks at nominal levels. The water leaving by crystals is not balanced as simply as that. For instance, using the process description above, it was stated that the pickle tank should be refilled with recovered acid and rinse water. This is to make up for the water removed by crystallization. To determine the amount needed on an accurate basis, consider the formula:

$FeSO_4.7H_2O$

molecular weights 152 + 126 = 278

This means that 45% of the weight of crystals produced is water removed. Therefore, if a plant removes 10 tons of crystals every 24 hours, 4.5 tons (or 1080 USG) of water must be added to the system every 24 hours, over and above of what is being added to make up for evaporation. Whether this is added as rinse water or fresh water in numerous small batches, or one big gulp needs to be determined by the prevailing process conditions, as long as it is added.

Keeping daily records of such things as:

Tank levels
Iron/acid concentration
Iron loss
Inhibitor additions
Crystal production
Water addition
Acid additions

will be a tremendous help in deciding how to keep the system in balance.

In a closed (effluent free system) the following observations need remedial action:

- -- if the iron content in the system is continually rising - means that either not enough crystals are removed or the steel throughput is more than the system can handle or the iron loss has gone up.

- -- if the liquid levels in the system are continually rising - means more water is being added than is being removed.

In both cases, the reverse is true also.

12.0 Garbage in the Process

If your pickling system is closed circuit, meaning totally effluent free, then the only materials leaving the process are water vapour to atmosphere and ferrous sulfate as crystals. Going into the process are also such things as graphite (carbon), silica, oils, dirt of all sorts, and many other insoluble materials. Some are from dissolving steel, some are brought in attached to the steel (paint, dirt, sand, oil) and some are brought in attached to pickle hooks (soap, lime, phosphate).

All these materials are retained within the system. Although they accumulate at a very slow rate, they are there and they are building up in the bottom of the tanks mostly, but some of the lighter ones are suspended in the solution (graphite). Eventually, say after 6-12 months of operation, the concentration of these tramp materials becomes such that it will cause problems in pickling, rinsing and recovery.

Owing to these potential problems, it is recommended that once every 6 to 8 months, a truck load of spent pickle liquor is hauled away, so as to provide a "blowdown" so to speak, just as in blowing down a boiler. It is also advisable that tanks, such as dunk rinse tanks, spent acid tanks and any other tanks where material has a chance to settle be scraped out at regular intervals to get rid of accumulated sludge.

Although most of the tramp materials trapped within the system are not controllable, it is advisable to try and keep those that are controllable out of the system: mud, sand, gravel, oil, paper, paint, wood. They all eventually break down in the acid to insoluble byproducts.

Your pickling system is a chemical process and as such processes specific chemicals. Therefore everything not related to the process must be kept out of open vessels and sumps, or eventually you will end up dealing with it with loss of production and loss of quality!

In Closing

It is nearly impossible to cover all areas of every and all sulfuric acid pickling facilities. Each operation has its own peculiarities. It is hoped, by this manual, to give enough insight into some of the most important aspects of pickling, to demonstrate that pickling is not just "cleaning" and that there are factual and physical explanations for everything.

More often than not, we find pickling people struggling with what appear to be incomprehensible problems, and spending a lot of unnecessary money and time to alleviate these problems in what appear to be sensible ways, only to find later they have just traded one problem for another. Many of these errors could be avoided, by consulting an unbiased third person who has no axe to grind and no position in the organization to protect and who can look at the situation objectively. There are such people available today in experienced engineering firms, which can handle any such problem and probably even improve performance of your process in general.

A pickling and recovery process can be clean, environmentally safe and a pleasure to operate; all it needs is someone to take care of it who has the basic background knowledge to understand what makes it tick. **You now have that knowledge so go to it and have a pleasant time doing it!**

ABOUT THE AUTHOR

Fred Hasler has been involved in acid related chemical systems since 1962. As a senior process operator with Dow Chemical of Canada Ltd., as a Process Superintendent with Peace River Mining and Smelting Ltd., as a Service Supervisor with KSF Chemical Processes Ltd., as an Operations Manager with David Krofchak Limited, as a Field Operations Manager with Ledge Engineering Inc., and at present as a Design Coordinator and Field Technologist with ESCO Engineering, his technological background originates with a Designers diploma specializing in Chemical process equipment design from Gebrüder Sulzer A.G. in Switzerland.

Since 1971 his hands-on experience with pickling and recovery systems using either hydrochloric or sulfuric acid has been constantly enriched by being intimately involved with the design, installation, operation and trouble shooting of numerous installations throughout North America.