The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

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INTRODUCTION

J. P. Kleingarn and company published a paper on spent acid regeneration in 1988. It made use of a graph, commonly referred to as the "Kleingarn Curve", which has become a guide in the acid regeneration practice of many galvanizing industries worldwide until now. It showed how to maximize the use of an already disposable acid by continuously adding fresh acid with or without fresh water to maintain high concentration with lowered iron content at optimum pickling time.

When mill scale and rust is dissolved in hydrochloric acid (HCl), the solution turns yellow to pale green indicating the presence of ferrous chloride (FeCl$_2$). Ferric chloride (FeCl$_3$) on the other hand exhibits a characteristic dark green to dark brown color. These salts remain dissolved until their respective solubility limits are reached wherein further addition of either salt will just form crystals that will settle to the bottom of the vessel or cling to anything suspended in the solution, including the steel being pickled.

Solubilities of ferrous and ferric chlorides are affected by water content, acid temperature, and acid concentration. The solubility value of ferrous chloride reduces as the water and acid concentration is increased and its temperature decreases whereas, ferric chloride solubility increases directly with the increase in acid concentration, water content, and temperature.

The increases in concentration of these acidic salts (pH's < 1.0 at about 40% by weight) seemingly provide added benefit by helping in the scale removal process. Ferric chloride is a known copper etchant and its contribution to steel pickling is akin to that effect. The salts' overwhelming presence however during the first regeneration procedure restricted effective free acid collision with iron and iron oxides resulting to either oxidation of ferrous chloride or reduction of ferric chloride that consequently increase pickling time outweighing its beneficial action on the rusted steel.

DEFINITION

Magnetite (Fe_3O_4)
- iron (II, III) oxide or ferrous-ferric oxide
- may also formulated as $FeO.Fe_2O_3$
- characteristic blue-black color
- also called the "black" oxide of iron

Hematite (Fe_2O_3)
- iron (III) oxide or ferric oxide
- rust
- also called the "red" oxide of iron

Wüstite (FeO)
- iron (II) oxide or ferrous oxide

Mill scale
- consists primarily of magnetite with significant amount of hematite (rust) on top, and elemental iron underneath

Mill scale with 80% magnetite ($FeO.Fe_2O_3$), thickness is 9.8 microns.

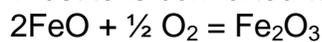Mill scale with 80% rust (Fe_2O_3), thickness is 50.8 microns.

Figure 1. Mill scale thickness comparison

MILL SCALE AND RUST REMOVAL BY HYDROCHLORIC ACID

Normally, slowly cooled hot-rolled steel coming from the production plant have a magnetite (Fe_3O_4) surface layer that protects it from corrosion unless the bond is broken. As the break comes in contact with atmospheric oxygen, the exposed inner iron and iron oxide oxidizes and the whole magnetite layer disintegrates into the following:

Magnetite coating = Wüstite • Hematite
Iron (II,III) oxide = Iron (II) oxide • Iron (III) oxide
Fe_3O_4 = FeO • Fe_2O_3

The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

Wüstite is converted to rust via the reaction:
$2FeO + \frac{1}{2} O_2 = Fe_2O_3$

Elemental iron oxidizes via the reaction: $Fe + \frac{1}{2} O_2 = FeO$

Correspondingly, magnetite (Fe_3O_4) reacts with the pickle acid giving FeO and Fe_2O_3 in the following proportions;

Consider: $Fe_3O_4 = Fe_2O_3 + FeO$, to get the respective weight values based on their atomic weights:

$[3(56) + 4(16)] = [2(56) + 3(16)] + [56 + 16]$
$[168 + 64] = [112 + 48] + [72]$
$232 = 160 + 72$

Therefore,
$Fe_2O_3 = (160/232)$ x $100 = 69\%$
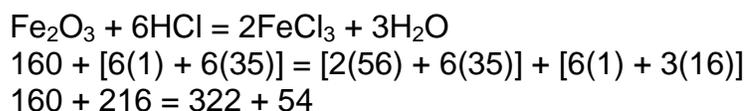$FeO = (72/232)$ x $100 = 31\%$

Average mill scale composition (actual raw materials for galvanizing as received):

- 15% Hematite or rust (Fe_2O_3)
- 70% Magnetite ($FeO.Fe_2O_3$)
- 15% Elemental iron (Fe) inclusive of base metal

PICKLING REACTIONS

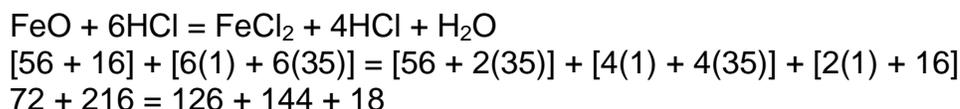A.1 Reaction of ferric oxide (Fe_2O_3) with hydrochloric acid

$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$
$160 + [6(1) + 6(35)] = [2(56) + 6(35)] + [6(1) + 3(16)]$
$160 + 216 = 322 + 54$

$322\ FeCl_3/216\ HCl = 1.491\ FeCl_3/HCl$
$54\ H_2O/216\ HCl = 0.250\ H_2O/HCl$

A.3 Reaction of ferrous oxide (FeO) with hydrochloric acid

$FeO + 6HCl = FeCl_2 + 4HCl + H_2O$
$[56 + 16] + [6(1) + 6(35)] = [56 + 2(35)] + [4(1) + 4(35)] + [2(1) + 16]$
$72 + 216 = 126 + 144 + 18$

$126\ FeCl_2/216\ HCl = 0.583\ FeCl_2/HCl$
$18\ H_2O/216\ HCl = 0.083\ H_2O/HCl$
$144\ HCl/216\ HCl = 0.667\ HCl/HCl$ (excess HCl/available HCl)

A.4 Reaction of elemental iron (inclusive of base metal) with hydrochloric acid

$$2Fe + 6HCl = 2FeCl_2 + 2HCl + 4H_{(gas)}$$
$$[2(56)] + [6(1) + 6(35)] = [2(56) + 4(35)] + [2(1) + 2(35)] + [4(1)]$$
$$112 + 216 = 252 + 72 + 4$$
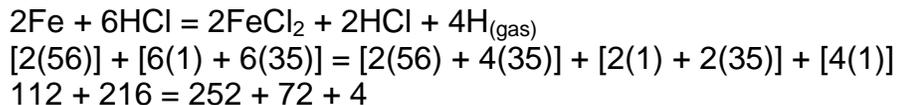
$252\ FeCl_2/216\ HCl = 1.167\ FeCl_2/HCl$
$72\ HCl/216\ HCl = 0.333\ HCl/HCl$ (excess HCl/available HCl)
$4\ H/216\ HCl = 0.018\ H/HCl$

Factors Affecting Pickling Rate

The time required in removing oxide and scale depends not only on the thickness and type of scale, but also on:

- Temperature of the bath
- Acid concentration
- Iron (II & III) concentration
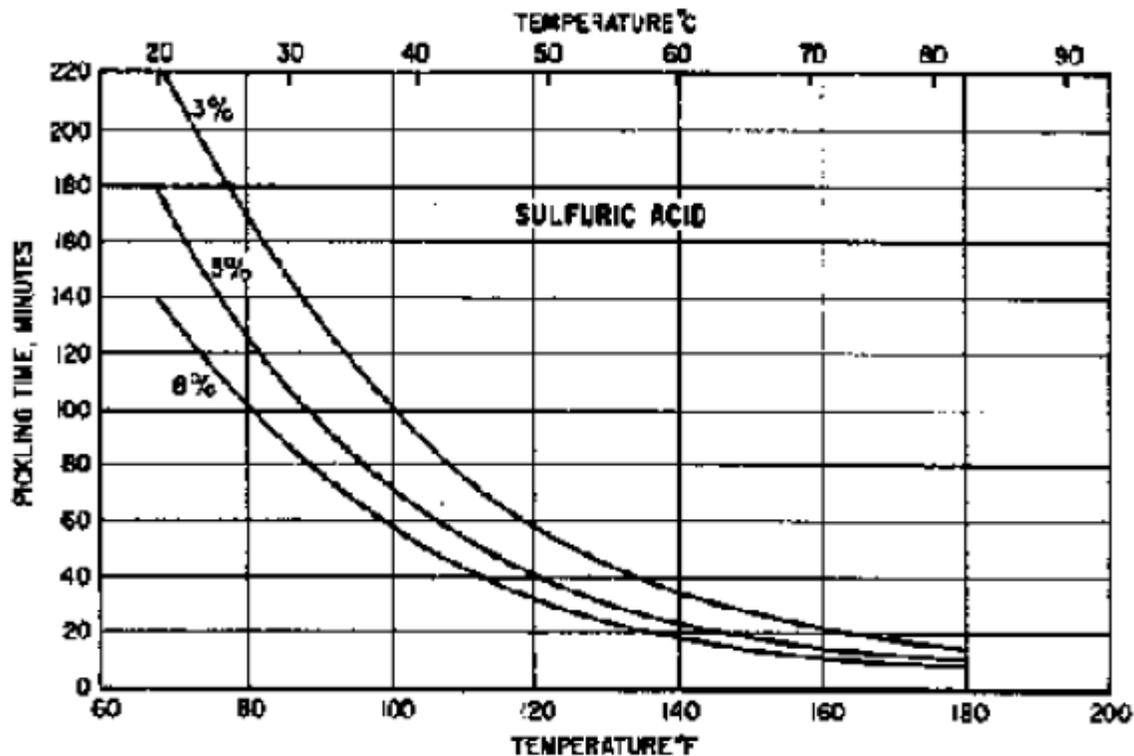- Agitation
- Inhibitor choice and concentration

Figure 2. Effect of Acid Strength and Temperature on Pickling Rate (Zaclon HB)

The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

Bench tests revealed that regenerated spent acid removes mill scale at a rate of about 2.0 kg/min compared to fresh acid of 2.5 kg/min both at initial concentration of 15% HCl and a steel weight to acid volume of 0.044 MT/M^3. This means that fresh acid pickles about 25% more than a regenerated spent acid. Ideally, pickling should remove scale and corrosion products of not more than 0.5 percent of the steel weight but often up to 1.0 percent is tolerated for steel with heavy rust.

SOLVING FOR WEIGHTS OF HCL TO FORM Fe^{+2} AND Fe^{+3} CHLORIDES

Data:

Hydrochloric acid pickle solution preparation: 15% HCl = 160 g HCl/~~Li sol'n.~~ x 68,000 ~~Li sol'n~~
    = 10,880,000 g HCl (available) for reaction
Volume of hydrochloric acid pickle solution:
    68,000 liters, assumed as final volume also excluding drag-out
Density of hydrochloric acid pickle solution: 1,050 g/liter

Thus,
- 10,880,000 g HCl used x 0.15
    = 1,632,000 g HCl used for Fe_2O_3 in rust
- 10,880,000 g HCl used x 0.70 x 0.69
    = 5,255,040 g HCl used for Fe_2O_3 in magnetite
- 10,880,000 g HCl used x 0.70 x 0.31
    = 2,360,960 g HCl used for FeO in magnetite
- 10,880,000 g HCl used x 0.15
    = 1,632,000 g HCl used for Fe (free + base metal)

Amount of free water in the hydrochloric acid pickle solution:
68,000 ~~Li sol'n.~~ x 1,050 g sol'n./~~Li sol'n.~~ = 71,400,000 g sol'n. (HCl + H_2O)
71,400,000 g sol'n. – 10,880,000 g HCl = 60,520,000 g H_2O (free)

THEORETICAL AMOUNTS OF Fe^{+2} AND Fe^{+3} CHLORIDES IN SINGLE-USE HYDROCHLORIC ACID PICKLE SOLUTION

I. HCl reaction with FeO
    i.   2,360,960 ~~g HCl~~ x 0.583 g FeCl$_2$/~~g HCl~~ = 1,376,440 g FeCl$_2$
    ii. 2,360,960 ~~g HCl~~ x 0.083 g H_2O/~~g HCl~~ = 195,960 g H_2O (free)
    iii. 2,360,960 ~~g HCl~~ x 0.667 g HCl/~~g HCl~~ = 1,574,760 g HCl (free)

II. Reaction with Fe_2O_3
    i.   (1,632,00 + 5,255,040) ~~g HCl~~ x 1.491 g FeCl$_3$/~~g HCl~~
        = 10,268,577 g FeCl$_3$
    ii. (1,632,00 + 5,255,040) ~~g HCl~~ x 0.250 g H_2O/~~g HCl~~
        = 1,721,760 g H_2O (free)

The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

III. Reaction with Fe
  i. 1,632,000 g̶ ̶H̶C̶l̶ x 1.167 g $FeCl_2$/g̶ ̶H̶C̶l̶ = 1,904,544 g $FeCl_2$
  ii. 1,632,000 g̶ ̶H̶C̶l̶ x 0.333 g HCl/g̶ ̶H̶C̶l̶ = 543,456 g HCl (free)
  iii. 1,632,000 g̶ ̶H̶C̶l̶ x 0.018 g H/g̶ ̶H̶C̶l̶ = 29,376 g H (evolved as gas)

a) Total free H_2O in the spent acid
60,520,000 g + 195,960 g + 1,721,760 g
= 62,437,720 g H_2O which is also the same as 62,437,720 ml H_2O

b) Total free HCl in the spent acid
1,574,760 g + 543,456 g = 2,118,216 g HCl

Express free HCl in concentration:
2,118,216 g HCl/62,438 liters free water
= 34 g/Li HCl which is about 3% HCl

c) Total $FeCl_2$ in the spent acid:
1,376,440 g + 1,904,544 g = 3,280,984 g $FeCl_2$

Express $FeCl_2$ in concentration:
3,280,984 g $FeCl_2$/68,000 liters spent acid solution = 48 g/Li $FeCl_2$

Fe/$FeCl_2$ = 0.44, hence Fe = 48 g/Li x 0.44 = 21 g/Li

d) Total $FeCl_3$ in the spent acid
10,268,577 g $FeCl_3$

Express $FeCl_3$ in concentration:
10,268,577 g $FeCl_3$/68,000 liters spent acid solution = 151 g/Li $FeCl_3$

Values of iron (from ferrous chloride) against hydrochloric acid concentration can be obtained using Fig. 3. Note that when the amount of magnetite coating is more intact in the raw material for galvanizing (lesser visible rust), the amount of ferrous chloride also increases.

When using the chart, project the amount of calculated iron from ferrous chloride analysis upward to the appropriate HCl concentration line by fresh acid preparation. At the intersection point, project a horizontal line to the left and read the value of the corresponding HCl concentration in % w/w.
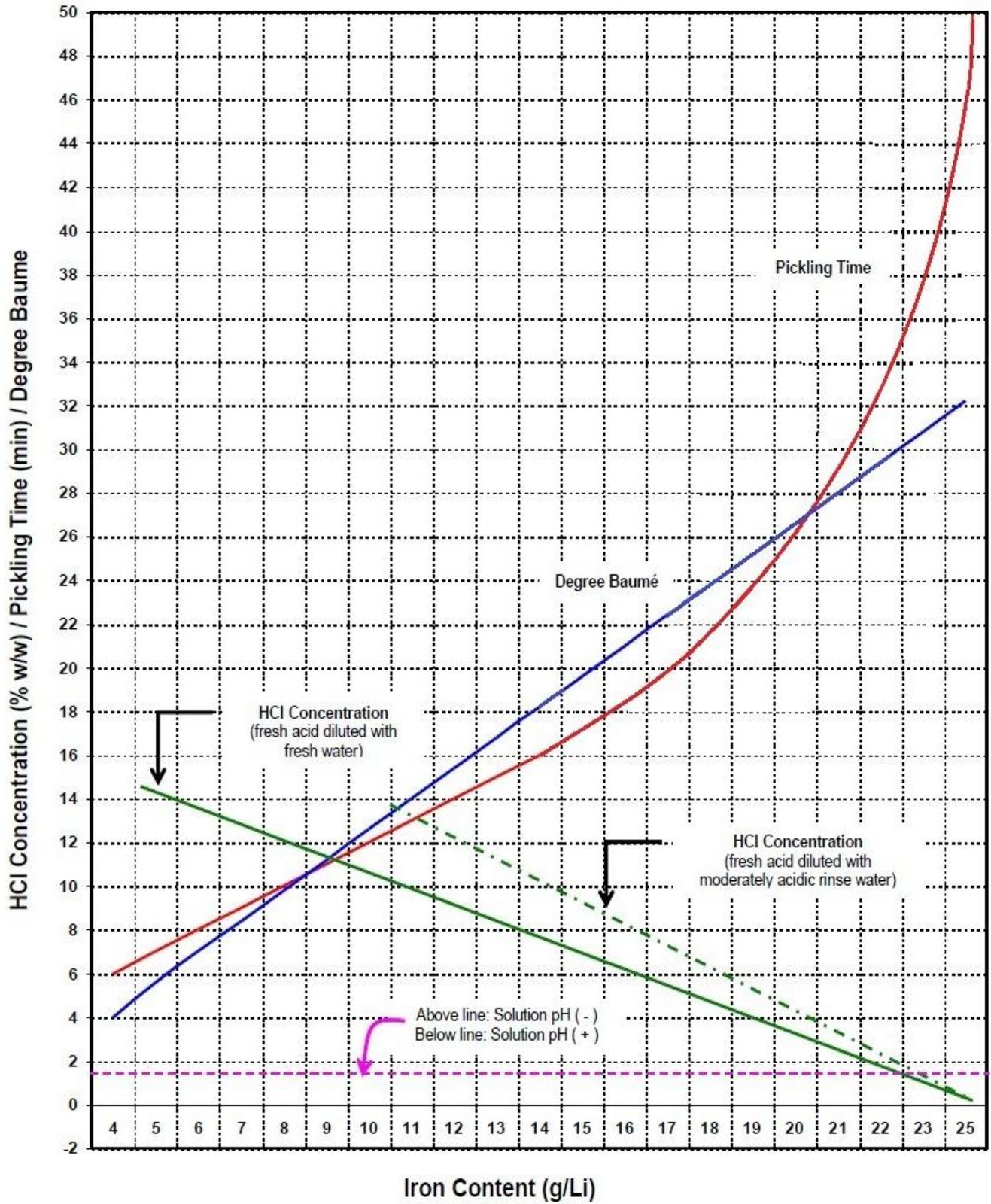
Figure 3. Hydrochloric acid pickling chart (www.finishing.com library)

The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

e) Solubilities of $FeCl_2$ and $FeCl_3$ in water

    i. $FeCl_2$

3,280,984 g $FeCl_2$/62,437,720 ml H_2O = 0.052 g $FeCl_2$/ml H_2O or equivalent to 5.25 g $FeCl_2$/100 ml H_2O

Solubility limit of $FeCl_2$ is 63 g $FeCl_2$/100 ml H_2O @ 20 ^{0}C, hence spent acid is not saturated with respect to $FeCl_2$.

    ii. $FeCl_3$

10,268,577 g $FeCl_3$/62,437,720 ml H_2O = 0.164 g $FeCl_3$/ml H_2O or equivalent to 16.40 g $FeCl_2$/100 ml H_2O

Solubility limit of $FeCl_3$ (hexahydrate) is 92 g $FeCl_3$/100 ml H_2O @ 20 ^{0}C, hence spent acid is not saturated with respect to $FeCl_3$.

THE KLEINGARN ACID REGENERATION PROCEDURE

The Kleingarn (K) Curve

The K curve (Fig. 4) assumed that a fresh pickle tank prepared with a concentration of about 16% HCl has no iron. Interpolating values found on Fig. 3, 16% HCl corresponds to about 172 g/Li HCl. The point of intersection between 172 g/Li HCl and 0 g/Li iron (left side value) of the curve lies well below the optimum pickling time (bold dashed line inside the shaded area). As pickling prospers, the iron concentration of the pickle solution increases and the acid concentration diminish. Kleingarn suggested that to do away with frequent preparation of fresh pickle acid, the spent acid may be regenerated by removing a certain amount of its volume and replacing it with either fresh hydrochloric acid or water.

The idea is to increase acid concentration of the spent acid and reduce its iron content in such a way it would still pickle fairly within the optimum pickling range that is below the optimum pickling time curve.

Please note that the values on the left y-axis (g/Li iron) and right y-axis (g/Li $FeCl_2$), vary significantly with the values found on Fig. 3. For example, Kleingarn's ideal pickling time line below the shaded area indicates that at about 94 g/Li (or 9%) HCl concentration, iron in the spent acid is about 50 g/Li corresponding to a ferrous chloride concentration of 110 g/Li. This is quite high compared to the corresponding iron content of 12 g/Li only for 9% HCl from Figure 3. It is thought that the probable cause of discrepancy is the differing methods of iron analysis.

The Hach FerroVer Iron method used in the analysis is USEPA approved for reporting wastewater analysis and reports iron as Fe from ferrous (Fe^{+2}) ions which in this particular

case is in the form of ferrous chloride. Ferric (Fe^{+3}) ions mostly will not be detected as it needs prior acid digestion in order to reduce it into the ferrous form.

HYDROCHLORIC ACID (AQUEOUS HYDROCHLORIC ACID SOLUTIONS)

Specific Gravity	Baumé	Per Cent HCl	Normality	Grams per Liter	Lbs. Per Cubic Foot	Lbs. per Gallon
1.0082	1.20	2	0.5528	20.16	1.2590	0.1683
1.0181	2.60	4	1.1170	40.72	2.5420	0.3399
1.0279	3.90	6	1.6910	61.67	3.8500	0.5147
1.0376	5.30	8	2.2760	83.01	5.1820	0.6927
1.0474	6.60	10	2.8710	104.70	6.5390	0.8741
1.0574	7.90	12	3.4800	126.90	7.9210	1.0590
1.0675	9.20	14	4.1000	149.50	9.3300	1.2470
1.0776	10.40	16	4.7280	172.40	10.7600	1.4390
1.0878	11.70	18	5.3700	195.80	12.2200	1.6340
1.0980	12.90	20	6.0220	219.60	13.7100	1.8330
1.1083	14.20	22	6.6860	243.80	15.2200	2.0350
1.1187	15.40	24	7.3630	268.50	16.7600	2.2410
1.1290	16.60	26	8.0490	293.50	18.3200	2.4500
1.1392	17.70	28	8.7480	319.00	19.9100	2.6620
1.1493	18.80	30	9.4560	344.80	21.5200	2.8770
1.1593	19.90	32	10.1700	371.00	23.1600	3.0960
1.1691	21.00	34	10.9000	397.50	24.8100	3.3170
1.1789	22.00	36	11.6400	424.40	26.4900	3.5420
1.1885	23.00	38	12.3800	451.60	28.1900	3.7690
1.1980	24.00	40	13.1400	479.20	29.9200	3.9990

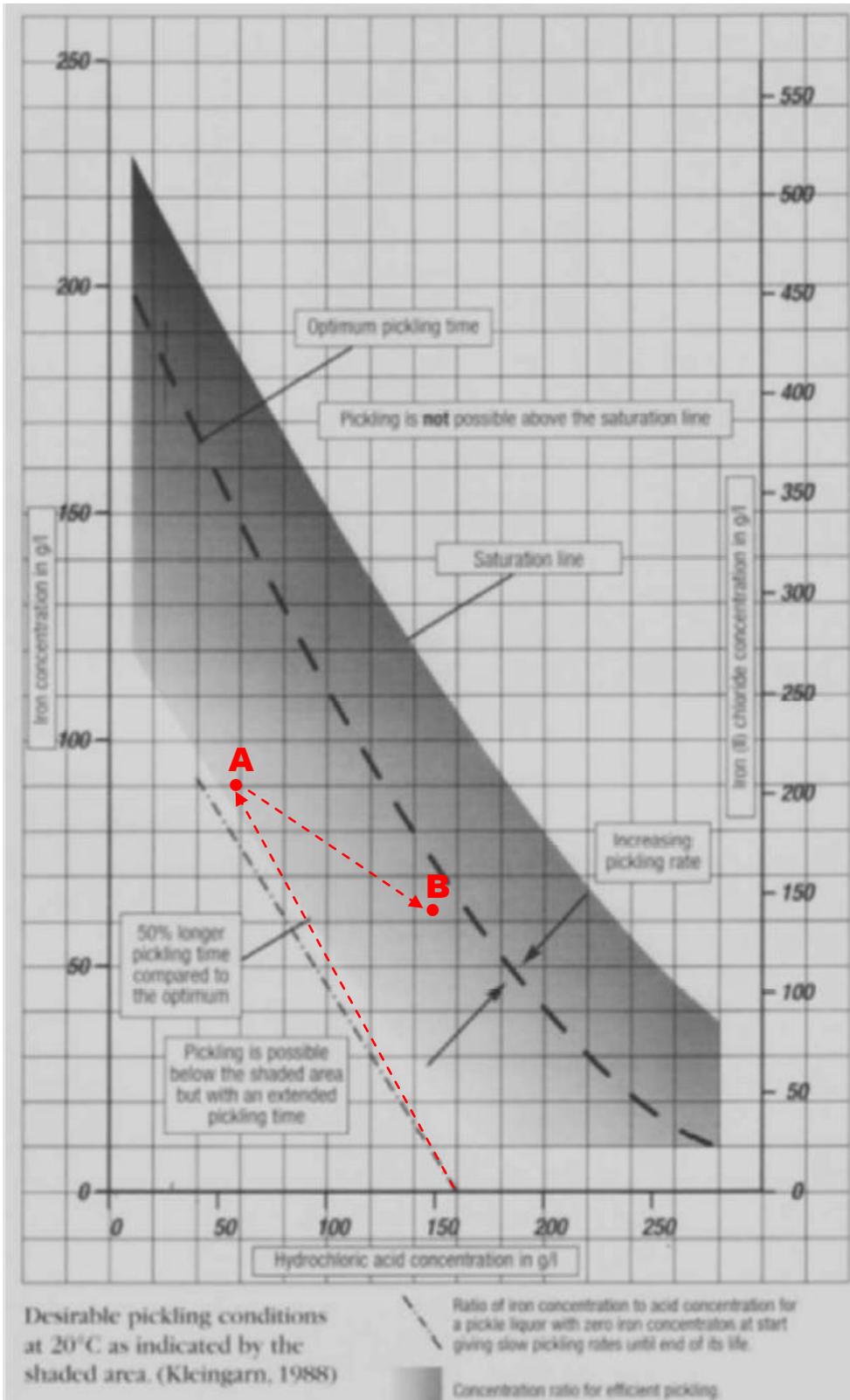**Figure 4.** Hydrochloric acid concentration table

Figure 5. The Kleingarn Curve

The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

Calculating that portion of spent acid to be removed and predicting the iron content of the regenerated spent acid

The following formulas were used to calculate the theoretical amounts of spent acid volume to be removed and replaced with fresh acid, and the expected iron content of the regenerated spent acid content where:

Y = volume of spent acid to be removed, M^3
Z = expected final iron conc. of regenerated spent acid, g/Li
a = target HCl conc. of regenerated spent acid, %
b = target volume of regenerated spent acid, M^3
a_1 = initial HCl conc. of spent acid, %
b_1 = initial volume of spent acid, M^3
c = conc. fresh acid, %
$d = (b - Y)$ = volume of remaining spent acid, M^3
d_1 = initial iron conc. of spent acid, g/Li
e = iron conc. of fresh acid = 0 g/Li

Equation 1:

$$Y = \frac{(a \times b) - (a_1 \times b_1)}{(c - a_1)}$$

Equation 2:

$$Z = \frac{(d_1 \times d) + (e \times Y)}{b}$$

For example: You may want to regenerate a 68 M^3 spent acid with 62 g/Li (6%) HCl and 90 g/Li iron contents. Plotting HCl and iron concentrations on the K curve yield an intersection point A within the shaded area below the optimum pickling time curve. By substituting values to the given equation:

$$Y = \frac{(14\% \times 68\ M^3) - (6\% \times 68\ M^3)}{(32\% - 6\%)}$$
$= 544\ \%M^3 / 26\ \%$
$Y = 21\ M^3$

$d = (68\ M^3 - 21\ M^3) = 47\ M^3$

$$Z = \frac{(90\ g/Li \times 47\ M^3) + (0\ g/Li \times 21\ M^3)}{68\ M^3}$$
$= 4{,}230\ g/Li\ M^3 / 68\ M^3$
$Z = 62\ g/Li$

The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

Plotting the new HCl concentration 150 g/Li (14%) and 62 g/Li iron content on the K curve would show the intersection point B still below the optimum pickling time curve thus the regenerated acid is still usable.

Nevertheless, experience tells us that there is already accumulated iron sludge inside the spent acid tank and we do not want that to react prematurely with the fresh acid and reduce its strength hence, what we do is use the following equation:

Equation 3:

$W = b_1 - Y$
   $= 68 \ M^3 - 21 \ M^3$
$W = 47 \ M^3$

Therefore, 47 M^3 of spent acid is to be removed from the upper portion of the tank into a previously cleaned tank and add the 21 M^3 of fresh acid there. Consequently, after the addition of about 0.2% (w/w) corrosion inhibitor/fume suppressant and thorough air mixing for about an hour, this now becomes your regenerated spent pickle acid.

FORECASTING THE REGENERATED SPENT ACID Fe^{+2} AND Fe^{+3} CHLORIDE CONTENT AND RESPECTIVE SOLUBILITIES

Basis:

Iron conc. in spent acid = 21 g/Li (from Fig. 1)
HCl conc. of spent acid = 2 %
Volume of spent acid = 68 M^3
Iron conc. in fresh acid = 0 g/Li
HCl conc. of fresh acid = 32 %
Density of fresh acid = 1.1593 Kg/Li

Solve for Y, d, Z, W using eqns. 1, 2, and 3:

$Y = \dfrac{(14 \ \% \ \times \ 68 \ M^3) - (2 \ \% \ \times \ 68 \ M^3)}{(32 \ \% - 2 \ \%)}$
   $= 544 \ \%M^3 \ / \ 26 \ \%M^3$
$Y = 27 \ M^3$ of spent acid to be removed

$d = (68 \ M^3 - 27 \ M^3) = 41 \ M^3$ spent acid remaining in the tank

$Z = \dfrac{(12 \ g/Li \ \times \ 47 \ M^3) + (0 \ g/Li \ \times \ 27 \ M^3)}{68 \ M^3}$
   $= 4{,}230 \ g/Li \ \cancel{M^3} \ / \ 68 \ \cancel{M^3}$
$Z = 8 \ g/Li$ iron in the regenerated spent acid

The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

$W = 68 \; M^3 - 27 \; M^3 = 41 \; M^3$ spent acid to be removed from the upper portion of the spent acid tank and transferred to a clean tank.

Data before spent acid regeneration:

Volume of spent acid for regeneration = 41 M^3 = 60% of the total regenerated solution
$FeCl_2$ in the spent acid = 3,280,984 g $FeCl_2$ x 0.60 = 1,968,590 g $FeCl_2$
Solubility $FeCl_2$ = 5.25 g/100 ml
$FeCl_3$ in the spent acid = 10,268,577 g $FeCl_3$ x 0.60 = 6,161,146 g $FeCl_3$
Solubility $FeCl_3$ = 16.40 g/100 ml
Free HCl in the spent acid = 2,118,216 g HCl x 0.60 = 1,270,930 g HCl which is about 3% HCl
Free H_2O in the spent acid = 62,437,720 g H_2O x 0.60 = 37,462,632 g H_2O which is also the
      same as 37,462,632 ml H_2O

Reactions during the addition of 21 M^3 fresh acid (32% HCl) where:

Weight HCl in the fresh acid:
32% HCl = 371 g HCl/~~Li sol'n.~~ x 21,000 ~~Li sol'n.~~
= 7,791,000 g fresh HCl

Weight fresh HCl solution of the fresh acid:
21,000 ~~Li fresh HCl sol'n~~. x 1.1593 Kg fresh HCl.sol'n./~~Li fresh HCl sol'n.~~
= 24,345 Kg fresh HCl sol'n.
= 24,345,000 g fresh HCl sol'n.

Weight fresh water in the fresh acid
24,345,000 g fresh HCl sol'n. = (7,791,000 g fresh HCl + g fresh H_2O) thus,
24,345,000 g fresh HCl sol'n. - 7,791,000 g fresh HCl = g fresh H_2O
= 16,554,000 g fresh water

Total weight HCl in the regenerated spent acid:
7,791,000 g HCl (fresh) + 1,270,930 g HCl (in spent) = 9,061,930 g HCl

Total volume water in the regenerated spent acid:
16,554,000 ml (fresh) + 37,462,632 ml (in spent) = 54,016,632 ml H_2O

Free HCl concentration in the regenerated spent acid:
9,061,930 g HCl/54,017 Li H_2O = 168 g/Li HCl

Interpolating g/Li HCl and % HCl values in Fig. 4 resulted to an acid concentration of about 16% HCl.

However, with reference to Kleingarn's equation no. 1, the computed volume of fresh acid added to the spent acid corresponds to an acid concentration of 14% HCl only which was verified true by actual concentration. This then means then that about 12.5% of the free acid in

the regenerated spent is lost and without a doubt through initial reaction with the dissolved iron and iron oxides.

Reaction of total HCl in the regenerated spent acid reaction with mill scale and rust:

- 9,061,930 g HCl used x 0.15
  = 1,359,290 g HCl used for Fe_2O_3 in rust
- 9,061,930 g HCl used x 0.70 x 0.69
  = 4,376,912 g HCl used for Fe_2O_3 in magnetite
- 9,061,930 g HCl used x 0.70 x 0.31
  = 1,966,439 g HCl used for FeO in magnetite
- 9,061,930 g HCl used x 0.15
  = 1,359,290 g HCl used for Fe

I. HCl reaction with FeO
   i. 1,966,439 g HCl x 0.583 g $FeCl_2$/g HCl = 1,146,434 g $FeCl_2$
   ii. 1,966,439 g HCl x 0.083 g H_2O/g HCl = 163,214 g H_2O (free)
   iii. 1,966,439 g HCl x 0.667 g HCl/g HCl = 1,311,615 g HCl (free)

II. Reaction with Fe_2O_3
   i. (1,359,290 + 4,376,912) g HCl x 1.491 g $FeCl_3$/g HCl
      = 8,552,677 g $FeCl_3$
   ii. (1,359,290 + 4,376,912) g HCl x 0.250 g H_2O/g HCl
      = 1,434,050 g H_2O (free)

III. Reaction with Fe
   i. 1,359,290 g HCl x 1.167 g $FeCl_2$/g HCl = 1,586,291 g $FeCl_2$
   ii. 1,359,290 g HCl x 0.333 g HCl/g HCl = 452,644 g HCl (free)
   iii. 1,359,290 g HCl x 0.018 g H/g HCl = 24,467 g H (evolved as gas)

   a) Total free H_2O in the regenerated spent acid
      37,462,632 g + 163,214 g + 1,434,050
      = 39,059,896 g H_2O which is also equal to 39,059,896 ml H_2O

   b) Free HCl in the regenerated spent acid
      1,311,615 g + 452,644 g = 1,764,259 g HCl

      Express free HCl in concentration:
      1,764,259 g HCl/68,000 liters regenerated spent acid solution
      = 26 g/Li HCl which is about 3% HCl

   c) Total $FeCl_2$ in the regenerated spent acid
      1,968,590 g + 1,146,434 g + 1,586,291 g = 4,701,315 g $FeCl_2$

Express $FeCl_2$ in concentration:
4,701,315 g $FeCl_2$/68,000 liters regenerated spent acid solution = 69 g/Li $FeCl_2$

$Fe/FeCl_2$ = 0.44, hence Fe = 69 g/Li x 0.44 = 30 g/Li

d) Total $FeCl_3$ in the regenerated spent acid
6,161,146 g + 8,552,677 g = 14,713,823 g $FeCl_3$

Express $FeCl_3$ in concentration:
14,713,823 g $FeCl_3$/68,000 liters regenerated spent acid solution = 216 g/Li $FeCl_3$

e) Solubilities of regenerated spent acid $FeCl_2$ and $FeCl_3$ in water

i. $FeCl_2$

4,701,315 g $FeCl_2$/39,059,896 ml H_2O
= 0.120 g $FeCl_2$/ml H_2O or equivalent to 12.00 g $FeCl_2$/100 ml H_2O

Solubility limit of $FeCl_2$ is 63 g $FeCl_2$/100 ml H_2O @ 20 ^0C, hence regenerated spent acid is still not saturated with respect to $FeCl_2$.

ii. $FeCl_3$

14,713,823 g $FeCl_3$/39,059,896 ml H_2O
= 0.377 g $FeCl_3$/ml H_2O or equivalent to 37.70 g $FeCl_2$/100 ml H_2O

Solubility limit of $FeCl_3$ (hexahydrate) is 92 g $FeCl_3$/100 ml H_2O @ 20 ^0C, hence regenerated spent acid is still not saturated with respect to $FeCl_3$.

Iron (II) and Iron (II) Chlorides	Solubility (g/100 ml)	
	Spent acid	Regenerated spent acid
$FeCl_2$	5.25	12.00
$FeCl_3$	16.40	37.70

Figure 6. Tabulated solubility results

Based on the above table, spent acid regeneration should be done only one time from the first preparation of pickle acid. Succeeding regeneration would saturate the regenerated acid thus pickling will eventually stop. If we are to correlate pickling time with the amount of iron chlorides present, the data tells us that pickling time doubles (x100%) during the first regeneration. In reality however, only about 25% increase in pickling time is fairly observed hence, the acidity of the iron chlorides therefore could have aided in the pickling process to a large degree.

Notable conditions were seen when using regenerated spent acid such as iron products clinging to the suspended steel and were very hard to wash away necessitating double rinsing.

Table 3
Comparison of Economics for a
Plant Pickling 100,000 TPY of Steel

BASIS: 1% iron loss; spent pickle liquor composition 8% dissolved iron, 8% H_2SO_4 all figures in thousands of dollars per year (1976 base)

Item	Basis	Acid Recovery	Neutralization	Contract Hauling
Investment	Figure	630.0	770.0	0
Salaries & Wages				
Operators	$12,500/man year	12.5	12.5	6.2
Foremen	$15,500/man year	1.5	3.8	0
Utilities				
Steam	$2.50/1000 lbs.	35.4	4.2	—
Process Water	$0.30/1000 gallons	(8.1)	—	—
Electricity	$0.02/kW·h	19.0	4.0	—
Raw Materials				
H_2SO_4	$50.00/ton	(50.0)	—	—
CaO	$32.00/ton	0	68.7	0
Shipping & Hauling Costs				
Crystals	$5.00/ton $FeSO_4 \cdot 7H_2O$	28.8	0	0
Sludge	$3.50/ton	0	110.0	0
Pickle Liquor	$0.14/gallon	0	0	350.0
Maintenance	6% of investment	37.8	46.2	—
General Plant Overhead	1.25 (wages & salaries + maintenance labor)	35.0	41.7	7.8
Waste Water Costs				
Sewer Fees	$0.40/1000 gallons	0	9.2	10.0
pH Adjustment	$2.50/1000 gallon rinse water	0	—	62.5
Taxes and Insurance	0.5% of investment	3.2	3.9	0
Depreciation	10% of investment	63.0	77.0	0
By-Product Credit	$10.00/ton $FeSO_4 \cdot 7H_2O$	(52.0)	0	0
Total Annual Costs		126.1	381.2	436.5

Rinse Water included in process water for acid recovery plants at 25 gal/ton pickled steel.

*Maintenance labor at 37% of maintenance cost.

Figure 7. USEPA Comparison Between Acid Recovery, Neutralization, and Contract Hauling

The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content

CONCLUSION

In consideration of very high spent acid disposal cost alone, Kleingarn's method is incomparable. Correlated solubility values of ferrous and ferric chloride showed that we can reduce as much as half the cost of spent acid disposal against a single-use pickle acid. This reduction in disposal cost however has to be evaluated against other major factors such as production, quality of product, and changes in overall chemical usage.

The significant reduction in spent acid disposal and fresh water addition comes with certain trade-offs which will make it more cumbersome and costly compared to single-use acid disposal, much more with the emergence of technologies such as vacuum distillation and membrane filtration/diffusion dialysis that have long been tested since the 1980's (Fig. 7) and were found to be cost-effective options in reducing if not eliminating wastewater generation through the recovery of acid and iron (which is more costly than the acid itself).

To highlight, costs of the following should be considered and quantified when opting to use the Kleingarn method:

- wastage of about 12.5% fresh acid due to initial reaction with iron contaminants already present in the spent acid solution
- compromised quality of product (red rust, brown stain, uneven coating, bare spots)
- reduced production output
- early deterioration of downline chemical solution tanks leading to:
    - increased rinse water usage and disposal
    - increased flux consumption
    - increased quench water usage
    - increased sodium dichromate consumption
    - increased ash and dross production
- Maintenance, labor, and energy

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