Acid Purification Chemistry
The Kleingarn Curve

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The Kleingarn Curve

The pickling of steel with hydrochloric acid is common practice in many industries. Pickling is performed to remove rust and scale so that uniform coatings (hot dip galvanizing, electroplating, powder coating, etc.) can be applied to increase the life of the coated part or fabrication. In the USA, approximately 50% of pickling is done using sulfuric acid and 50% with hydrochloric acid. The focus of this paper is to review the Kleingarn Curve and discuss how this curve can be utilized with a novel chemistry that precipitates soluble iron and zinc from hydrochloric acid. Continuous purification of HCl improves pickling speed and the quality of the product in addition to minimizing or eliminating disposal waste material.

Prior to the 21st century, a galvanizer had the following disposal options for partially spent HCl solutions.

- On-site Neutralization
- Off-site Disposal – Deepwell, Neutralization
- Off-site Beneficial Reuse – PVS Technologies, Kemiron, Municipalities

The costs and liability for off-site disposal/reuse options are increasing. Hence, a chemical process introduced in 2000 to the electroplating industry offered a cost effective viable option to the problem. The chemistry underlying this process was first used by the galvanizing industry in Canada in 2003 and continues to be used there today. The chemical technology is also used currently in the USA, Australia, Chile, Turkey, Romania and Singapore.

The Kleingarn Curve

J. P. Kleingarn with VDF published a paper[3] in 1988 that translated prior "scientific results into the language of the practical man." Dissolving rust and mill scale in HCl produces ferrous chloride, ($Fe\ Cl_2$) which is green. Ferrous chloride is soluble in HCl within restricted limits depending upon temperature and concentration. Exceeding the maximum solubility causes the precipitation of ferrous chloride crystals and stops the pickling reaction. The solubility limit for iron and iron chloride is reduced as the acid concentration increases and the temperature decreases.

The basis for control with the Kleingarn curve is the addition of either water or acid to reduce the iron concentration so that the concentration falls on the optimum pickling line or well within the shaded areas as illustrated in Figure 1. The addition of water or acid means that some volume of partially spent acid must be removed to make room for the added acid or water. This

decanted solution is now a hazardous waste which must be handled in accordance with RCRA (Resource Conservation and Recovery Act) regulations or similar regulations enforced in other countries.

From Germany to the USA (English Units)

Galvanizers in the USA, Canada and Mexico generally report the HCl and iron concentrations in %. The K curve is in g/l. An easy way for the "practical" man is to do the following:

1. Assume titrations give 10% HCl and the hydrometer reading for specific gravity is 1.2.
2. 10% HCl = 104.7 g/l HCl from Table 1
3. Refer to Figure 2 Nomogram. At 104.7 g/l HCl and sp. gr. of 1.20, the solution contains 78 g/l Fe.
4. Refer to the K curve with these values. The point falls within the shaded area. The additional of 35 g/l of HCl will move the point to the right on the optimum pickling time line.

The Acid Purification Chemistry

Industry has long desired a technology that would continuously remove iron (and zinc) from a pickling solution (whether HCl or H_2SO_4) without the need to decant or dump the pickle bath. A chemistry based upon catalyzed sodium silicate, used in conjunction with appropriate filtration, has been proven to reduce iron and zinc concentrations in all types of acids.

Referring back to Figure 1, one can see that a solution containing 100 g/l Fe and 170 g/l HCl is at the saturation line and no longer suitable for pickling. To return to the optimum pickling line without decanting, it would be necessary to reduce the iron concentration from 100 g/l to 60 g/l. In a 5,000 gal pickle tank, this would require the removal of 40 g/l Fe or 1,667 lb of Fe. Over a relatively short period of time (less than one to two weeks), the chemistry and filtration would remove this amount of iron as a combination of elemental iron, iron silicate and iron chloride. The removal of 1,667 lb of iron would result in approximately 1.2 yd^3 of non-hazardous filter cake.

An opposite situation could occur when the acid tank contains 50 g/l Fe and 100 g/l HCl. According to Figure 1, the pickling time would be 50% longer than optimum. The operator has the following options when using the chemistry depicted in this situation:

- Add acid to raise the bath acid concentration to 170 g/l HCl

- Turn off filtration system and allow iron concentration to increase to 110 g/l

Filtration Options

A filtration system must be installed to remove the precipitate formed in the process. Factors that affect the type of filter selected include:

Tons of steel pickled per day	Capital cost comparisons
Disposal of filter media	Operating labor
Size of pickle tanks	Concentration of organics
Availability of Waste Water Treatment	

From 2000 to 2006, cartridge filter systems of various sizes combined with the chemistry have been used successfully. The capital cost is relatively low but operating costs for labor, cartridge purchase and cartridge disposal are relatively high. The metals in the sludge often pass TCLP but the cartridges must be handled as a hazardous waste unless the retained acid is neutralized with caustic or lime. A safety concern is that operators are exposed to the acid while filters are changed. Figure 3 shows a typical cartridge filter.

In 2007, as the galvanizing, steel pickling and wire industries began to accept the chemistry, more sophisticated filtration systems have been installed (Figures 4 and 4A). An automatic backpulsing filter is sized to turn the baths over every 1 to 3 hours. The filter system automatically purges unfiltered acid prior to the backpulsing step. A small quantity of water and air is used to flush the solids from the filter into a backwash holding tank. From there the solids are dewatered in a conventional filter press. The solids in the filter press cake are non-hazardous. Figure 5 shows a Global filter installed in a galvanizing plant and Drawing 1 shows the complete treatment system. If the galvanizing plant does not currently have a good flux filtration system, the filter press, with proper piping, can be used for flux filtration when not required to remove the iron/zinc precipitates contained in the Global backwash water.

Figure 6 illustrates a gravity type bag filtration system installed at a galvanizing plant in June 2007 to remove metal precipitate from an 11,000 gal HCl pickle tank. Initial reports from the customer are favorable. The filter has 40 bags with a total capacity of 40 ft^3.

The PRO-pHx Chemistry

The liquid product is used as follows:

- Initial fill: 1% of tank volume
- Operation: Ratio 1 : 100 Product : acid spike

No new analytical test is required as the process is monitored by testing for iron and acid concentrations.

Economic Benefits

The chemistry is presently being used in 20 galvanizing plants worldwide because the chemical technology and filtration provide both economic and environmental benefits. Tables 3 and 4 illustrate these benefits.

Economics

Country	Chile
HCl volume, gal	31,700
Treatment time, mo	27
Net Savings, $/Yr	107,000
Previous Dump Frequency weeks	4 – 6
Present Dump Frequency	NONE
Steel Pickled, Tons/Yr	24,000

Table 3

Economics

Country	USA-captive shop
HCl Volume, gal	9,500
Treatment Time, mo	8
Net Savings, $/Yr	31,000
Previous Dump Frequency/mo	2 – 3
Present Dump Frequency	NONE
Steel Pickled, Tons/Yr	15,000

Table 4

Summary and Conclusions

The chemistry introduced to the galvanizing industry in 2003 has proven to be an economic and environmental success at all plants using HCl. When the chemistry is utilized with proper filtration, the galvanizing plant can anticipate:

- A 30% reduction in virgin acid purchases
- Eliminate hauling of a hazardous waste
- Improved and consistent pickling speed and quality
- Reduced flux maintenance
- Reduced production costs
- Improved operator safety

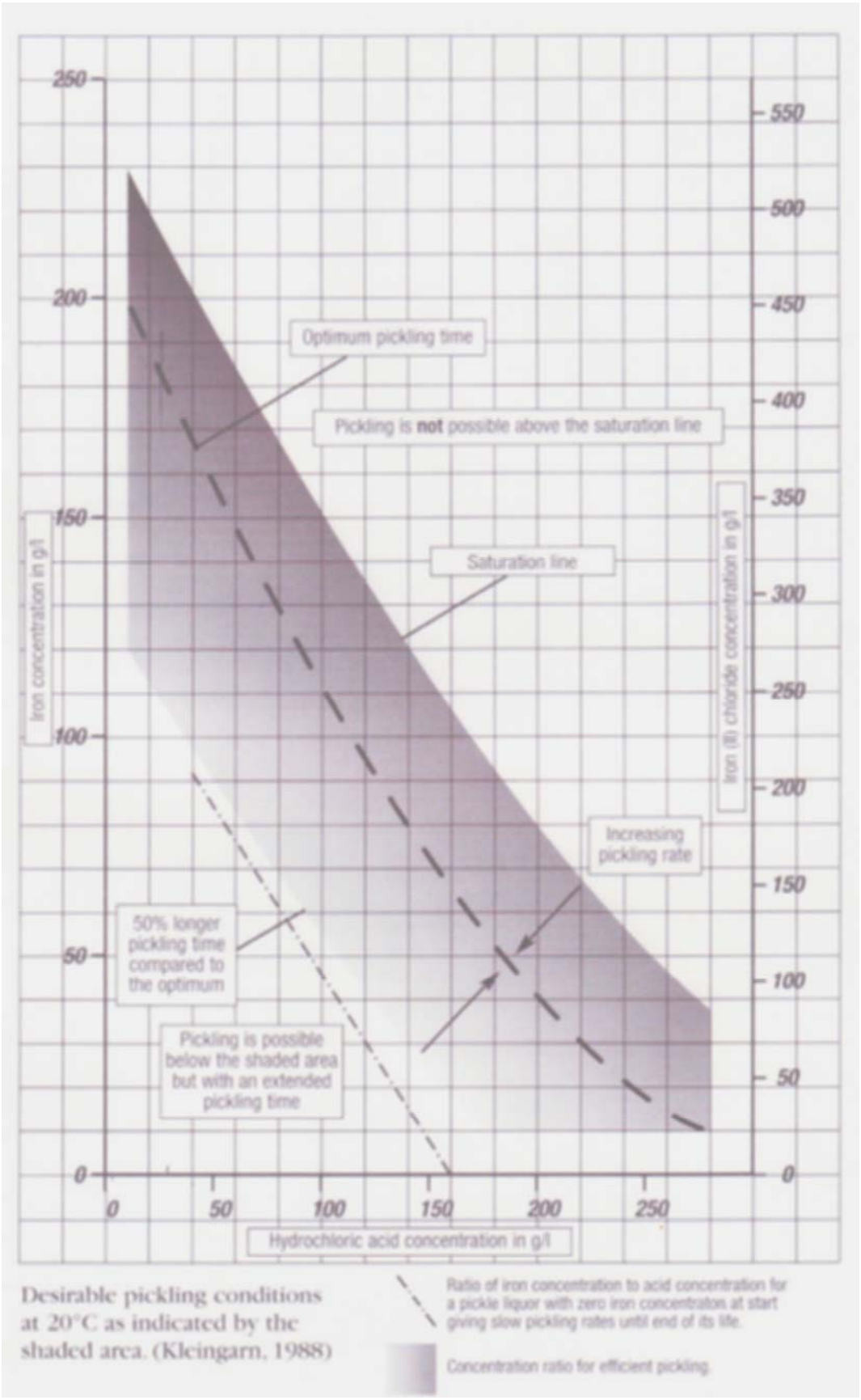
All state regulatory agencies that have been contacted have recognized the PRO-pHx chemistry as Pollution Prevention Technology. Many states provide tax incentives for the equipment used in P^2 projects.

References

1. Stone, N., "Pickling Science: Not a Black Art," Wire Expo 2002, Chicago, IL

2. Meathen, B, Arnesen, IH and Engell, H.J., "The hydrochloric acid/iron chloride/water system and the behavior of hot rolled steel strip during pickling in solutions of this type," Stahl und Eisen, 1965, 85(26), 1722-1729

3. Kleingarn, J.P., Intergalva 1988, EGGA



Desirable pickling conditions at 20°C as indicated by the shaded area. (Kleingarn, 1988)

Figure 1

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

Table 1

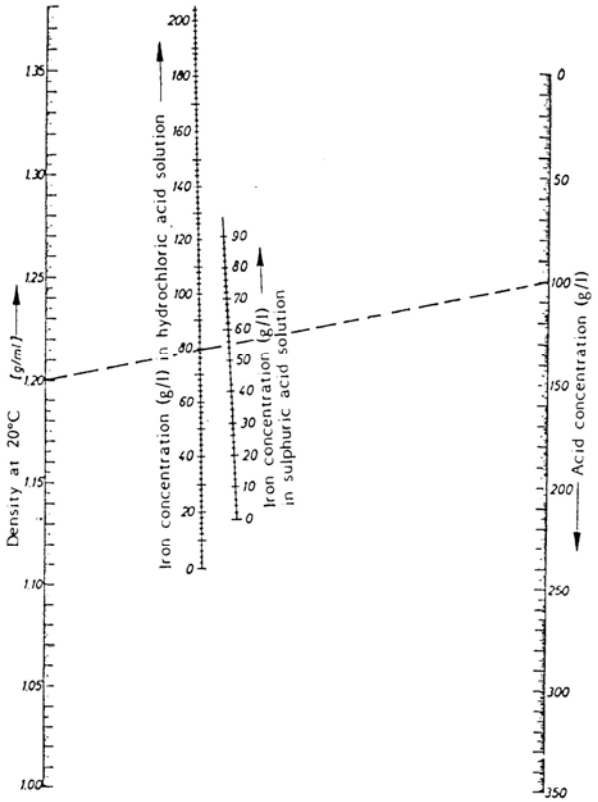


Figure 2: Nomogram for the density of hydrochloric acid or sulphuric acid solutions containing iron (II) salt at 20°C.

Figure 3
Cartridge Filter

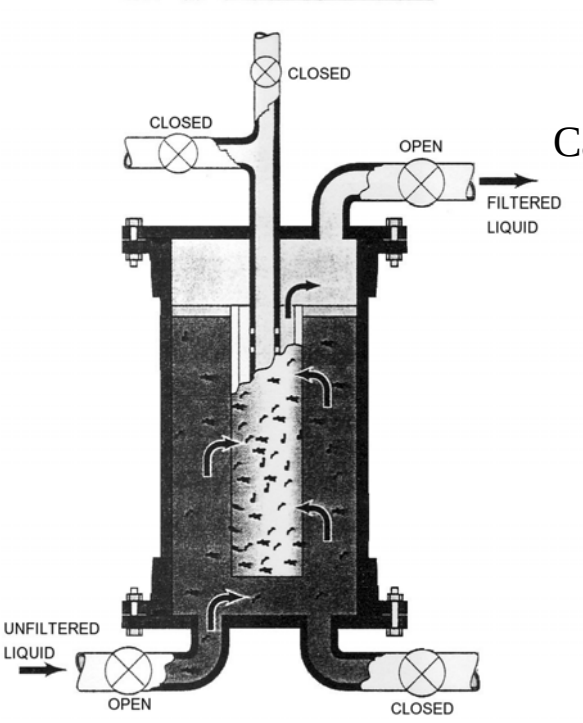


Figure 4
Service Cycle

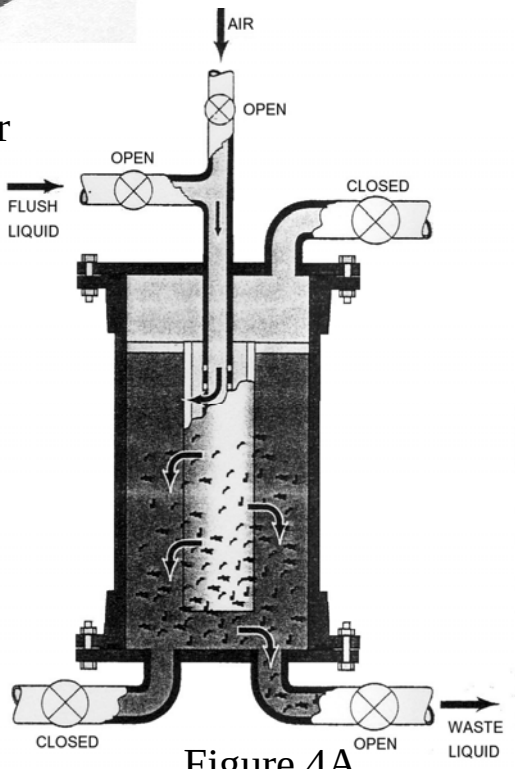


Figure 4A
Backpulse Cycle

Figure 5
Global Filter

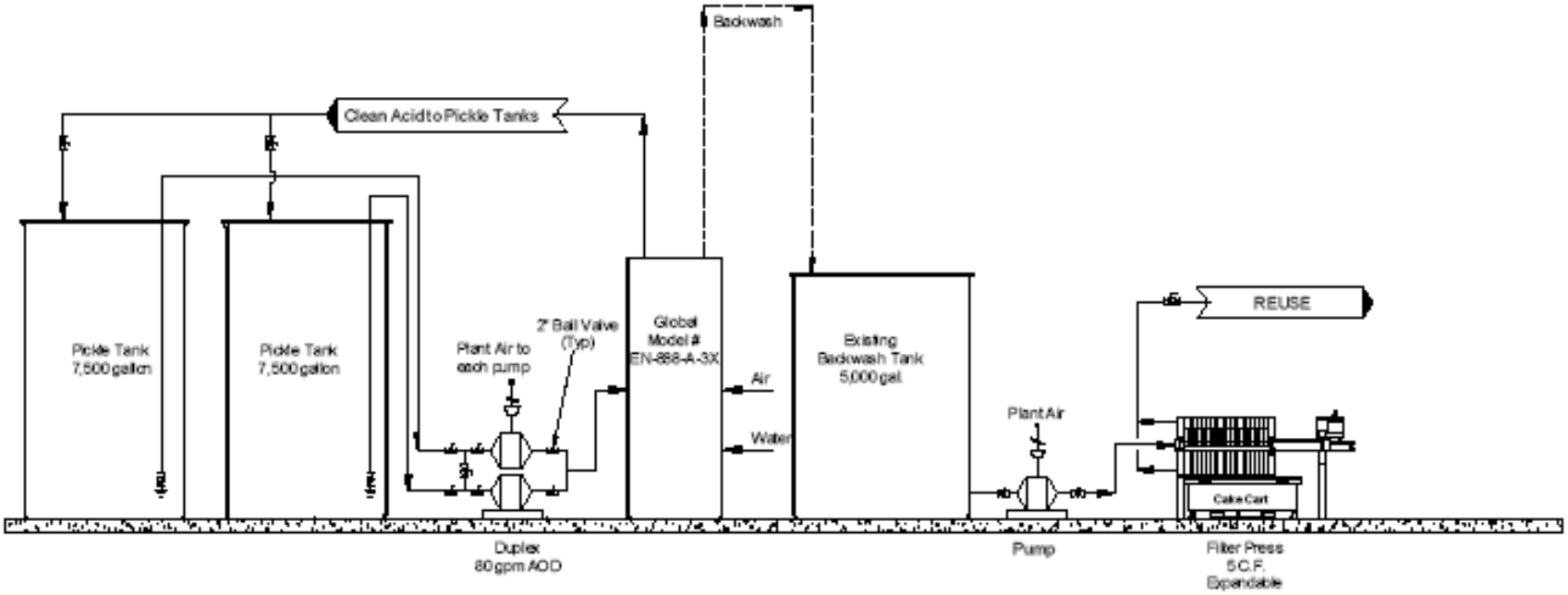
Drawing 1

Acid Type: HCL

Acid Temp: AMB

Total Acid Volume: 2-7,600 gallon

Filtration Rate: 160 GPM



Notes:

1. The addition of a mixer and chemical feed pump to the backwash tank allows the system to handle rinse water dumps.
2. Filter Press can be used for Flux Filtration

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PRO-pHx

1246 Rock Creek Road
Hot Springs, AR 71913

DWG. NO.	1
OF	1
	Filtration/Solids Dewatering System
	Pro-pHx Treated Acids
	Universal Form Clamp
JOB NO.	07-036A
LAST UPDATE	8/21/07
DWG FILE	07-036-016-CA75
DATE	8/21/07
SCALE	NONE
DRAWN BY	RCB
CHECKED BY	CTP

Bag Filter
Figure 6