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Steel Pickling in Challenging Conditions

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<p>The purpose of this thesis was to collect data on the pickling procedure and parameters especially in conditions where there are limited amount of power for heating, limited water treatment possibilities and equipment to maintain pickling processes.</p> <p>Information about steel pickling, alternative methods and processes before and after pickling was acquired. Data on most common chemicals for pickling were acquired and compared. Cleaning efficiency, ease of use, safety, price and availability of acids were taken into account in comparison. Information regarding especially citric acid was gathered as suitability for these conditions needed to be confirmed.</p> <p>Citric acid, hydrochloric acid and phosphoric acid were selected to be the best options. They were tested on carbon steel tubing at varying temperatures and concentrations. Pickling efficiency was measured by weight loss method. Weight loss - temperature figures were drawn for each tested chemical. Rinse water temperature efficiency measurement was attempted by titration of residual acid. Acid inhibitor efficiency was measured and compared between formalin, Stannine LTP, succinic acid and eucalyptus oil.</p> <p>Citric acid is an excellent option in cases where ease of use and safety is valued higher than short pickling time. Comparable data between hydrochloric, citric and phosphoric acid should be helpful when deciding between chemicals. Inhibition and agitation effect on citric acid pickling could be studied further to provide a more optimized process guide.</p>	
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<p>Insinöörityön tavoitteena oli kerätä tietoa peittäusprosessista ja siihen vaikuttavista tekijöistä. Työssä keskityttiin olosuhteisiin, joissa on rajoitetut lämmitys- ja vedenkäsittelymahdollisuudet eikä erikoislaitteistoja peittäusta varten.</p> <p>Tietoa kerättiin peittäuksesta, vaihtoehtoisista menetelmistä ja esi- sekä jälkikäsittelyistä. Työssä tarkasteltiin yleisimpiä kemikaaleja ja niitä vertailtiin tehon, käytävyyden, turvallisuuden, hinnan ja saatavuuden suhteen. Tiedonkeruuta painotettiin sitruunahappoon, koska sen soveltuvuudesta näihin olosuhteisiin oltiin kiinnostuneita.</p> <p>Sitruunahappo, suolahappo ja fosforihappo valittiin tarkempaan vertailuun parhaina vaihtoehtoina. Kyseisten happojen tehoa vertailtiin peittaamalla hiiliteräsputkea eri lämpötiloissa ja eri konsentraatioilla. Peittäustehoa vertailtiin painohäviön perusteella. Testatuille kemikaaleille piirrettiin kuvaajat. Huuhteluveden lämpötilan vaikutusta happojäämiin pyrittiin mittaamaan titraamalla kappaleiden happojäämiä. Inhibiittien tehoa mitattiin formaliinin, Stannine LTP:n, meripihkahapon ja eukalyptusöljyn välillä.</p> <p>Kerätyn tiedon ja suoritettujen kokeiden perusteella todettiin sitruunahapon soveltuvan peittäuskemikaaliksi erityisesti silloin, kun haluttiin painottaa helppokäyttöisyyttä ja turvallisuutta lyhyen peittäusajan sijaan. Eri happoja koskeva vertailukelpoinen tieto tukee peittäuskemikaalien valintaa haastavissa olosuhteissa. Lisäaineiden ja sekoituksen vaikutuksen selvittäminen vaatisi lisätutkimusta optimoidumpien suositusten saavuttamiseksi.</p>	
Avainsanat	peittäus, teräs, sitruunahappo, inhibiointi

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1 Introduction

The purpose of this thesis was to collect data on the pickling procedure and parameters especially in conditions where there are a limited amount of power for heating, limited water treatment possibilities and limited equipment to maintain pickling processes.

In a continuous pickling line, processes can be highly optimized and expensive equipment pays for itself quickly. Stronger acids and higher temperatures can be used in the pickling process to provide faster pickling times. Most of the literature only discusses pickling in pickling plants and the optimization of pickling in continuous pickling lines. Although a variety of chemicals is mentioned regarding steel pickling, more specific data is available only for hydrochloric and sulfuric acid. Information on less commonly used chemicals is scattered and very application-specific.

Information was collected to build an overview on the steel pickling process and the variables affecting it. Acid specific data was collected to compare their environmental, efficiency and price differences. After choosing the best acids, tests were run in order to achieve comparable data between chemicals to help understand the differences. In addition, different inhibitors were compared and tested to give comparable data.

The objective was to provide a document that would answer most of the questions regarding steel pickling processes and acids. Determination of efficient temperature range and inhibition usage were the main objects of interest.

2 Steel Pickling

Metal surfaces can contain multiple kinds of impurities that could affect usage or coating of the product. Usually these are oxides, hydroxides, cutting oils, rust prevention oils, greases, casting sand, organic compounds, salts and welding spatter. Impurities can be removed by chemical or mechanical methods. Pickling is the most common method to clean steel products. [1, 114; 2, 170]

Pickling is defined as a chemical or electrochemical process in which surface oxides are removed from metal. The exact definition varies; sometimes steel pickling is defined as removal of mill scale, and acid cleaning is defined as final or near-final process. [3, 48; 2, 459]

Pickling process usually contains three stages. During pre-cleaning oils, greases and salts are removed. It is followed by pickling where oxides are removed using acid mixed with additives. When surfaces are clean, rinsing and possible neutralization follow to remove acid residues. Additional rinsing between these steps can be used to prevent bath contamination and reduce chemical consumption. Figure 1 shows the cleaning effect of pickling. [1, 114-122; 3, 52]

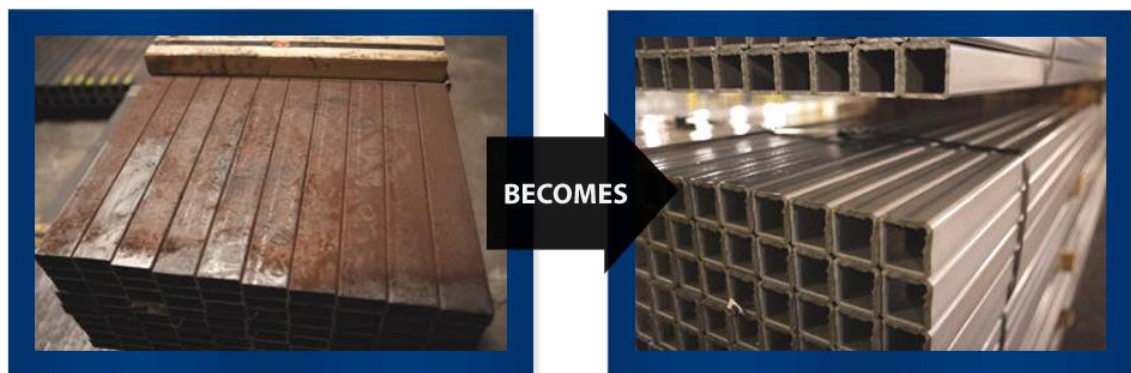


Figure 1. Before and after photo of pickling. [4]

2.1 Pre-Cleaning

Degreasing must be performed to allow proper function of pickling. Degreasing is usually performed within a hot alkaline bath. Surfactants and solvents can be in mixtures or alone. Waxes and greases are removed more effectively at 60–90 °C. Pre-

cleaning procedures must be chosen on a case-by-case basis depending on the type of impurities. [3, 69-70; 5, 24]

2.2 Pickling

2.2.1 Oxide Layer

Oxide layer forms on steel during manufacturing and hot-working when surface reacts with oxygen in the air. The composition of the formed oxide scale depends on the cooling rate. With fast cooling rate easily soluble wüstite (FeO) is retained on the surface. If cooling time is long wüstite transforms into magnetite (Fe_3O_4) and iron. Magnetite and the thin outermost layer of hematite (Fe_2O_3) dissolve slowly. [3, 67; 1, 116-122]

The composition of steel has little or no effect on oxide layer structure, but steel with high carbon or manganese concentration shortens the pickling time required. Silicon content extends the required pickling time. [1, 116]

2.2.2 Pickling Mechanism

Pickling acid penetrates magnetite and hematite layers through cracks and reacts with wüstite layer as shown in Figure 2. Acid also reacts with the base metal and hydrogen gas is formed. Gas bubbles assist the detaching of the magnetite layer and speeds up the process. [3, 67-68; 5, 9]

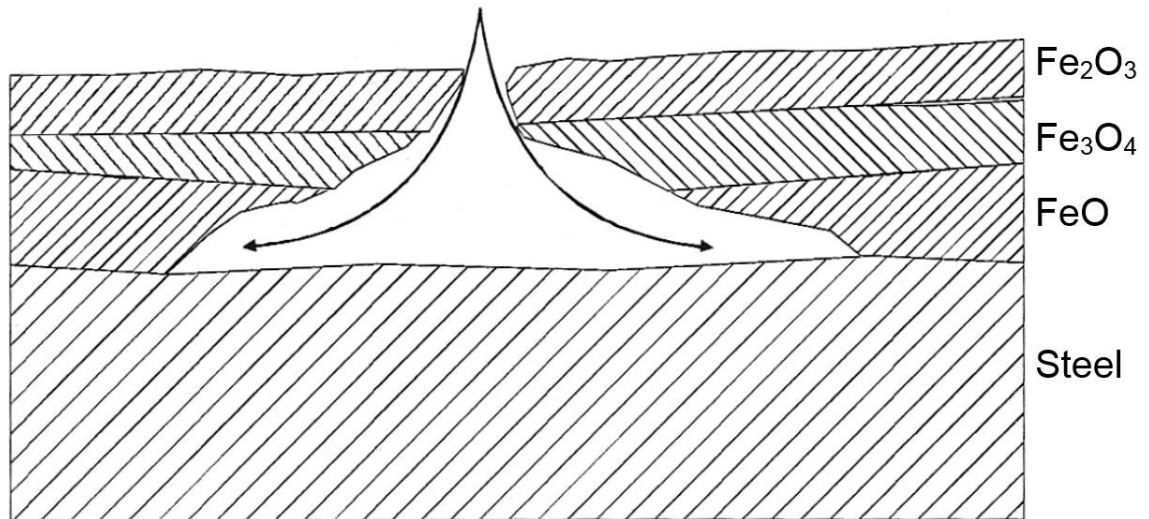


Figure 2. The mechanism of pickling. [1, 9]

2.2.3 Inhibition

The reaction between base metal and acid is not desired. Over-pickling may lead to a mechanical failure and the reaction increases acid consumption. Formed gas might also cause hydrogen embrittlement in high-strength steels with hardness over 33 HRC. [3, 69; 1, 111-118]

Inhibitors may operate in three different ways. Film forming inhibitors form a thin layer over the base metal and stop the reaction. Cathodic inhibitors slow the reaction kinetics of the cathodic reaction and anodic inhibitors slow anodic reaction. Mixed inhibitors slow both reactions. Often inhibitors work in multiple ways depending on the conditions. Commercial pickling inhibitors are usually mixtures of wetting agents and organic synthetic compounds. Even a small addition of pickling inhibitor to a solution (0.1–2.0 %) can reduce corrosion by 99%. Efficiency depends on the material, acid and temperature. Higher concentrations do not increase efficiency after a certain level and can affect the pickling process. For strong acids (HCl and H₂SO₄), inhibition is required, and for other acids, it must be considered on a case-by-case basis. [6, 1; 7, 845; 2, 171]

Active ingredients are usually organic compounds containing nitrogen, phosphorus, arsenic, oxygen, sulphur and selenium. Inhibitor compounds that contain multiple bonds tend to be more effective. Originally natural products such as tar were used, but

aldehydes, amines and acetylene alcohols have replaced them. Studies have shown that environmentally friendly alternatives like plant extracts could be used for acid inhibition. [7, 839; 3, 69; 8]

2.2.4 Other Additives

Wetting agents are used to reduce surface tension and to dissolve impurity residues that could affect the pickling. Some surfactants also create foam to reduce solution evaporation. Antifoaming agents may be added if foaming is not desired. [1, 119; 3, 48-49]

2.2.5 Factors Affecting Pickling Efficiency

Sufficient amount of time is the most important thing in order to achieve proper pickling result. The pickling time varies since the dissolution of oxides takes time and structure of the oxide layer can vary. Excessive time should not be used because over-pickling could occur. Over-pickled surface becomes uneven and porous because acid attacks grains and grain boundaries at different speeds. [3, 69; 1, 111-118]

Heating accelerates pickling reactions, but it also increases health risks by vaporizing acids. In addition, more inhibitor is needed to protect the base metal sufficiently. Energy consumption and hazards in working conditions usually limit heating. [1, 117-122; 9, 2-4; 10, 8]

Flow rate and mixing is difficult to relate directly to the pickling result. Mixing keeps concentrations even and the reaction going. Turbulent flow increases pickling speed explicitly. The advantage of turbulent flow is commonly used only in continuous pickling lines because special equipment is needed. Ultrasonic pickling can also be used to reduce pickling time. Air bubble agitation is generally used. [1, 118; 2, 172; 11, 111-112; 12, 90; 13, 19]

Higher acid concentration increases pickling efficiency mainly in cool temperatures. In elevated temperatures the difference is smaller. High concentrations might be limited by chemical consumption, fumes and acid contaminated rinsing water. [1, 117-122]

2.3 Rinsing and Neutralization

After the pickling process is finished, the parts must be rinsed with water to remove any acid residues that could cause corrosion later on. Surfaces should be dried rapidly to avoid flash-rusting. This can be achieved by using heated water and compressed air. Heated water, wetting agents and mixing can be used to provide better rinsing effect. Alkaline solution can be used to neutralize acid residues. [3, 52; 12, 92]

3 Other Types of Pickling

3.1 Stainless Steel Pickling

Impurities on stainless steel surface can be removed by pickling. Welding and heat treatment cause stainless steel to oxidize and under the oxide layer a chromium depleted layer is formed. These layers must be removed to restore corrosion resistance. Passivation can be performed after pickling to ensure the proper film formation of chromium oxide. [14, 5; 15, 9]

Pickling pastes can be used to pickle smaller areas. Stainless steel pickling requires hazardous chemicals and may thus need special equipment. Chemicals should be separately chosen for different alloys to provide proper cleaning effect. Pickling is the best method to restore corrosion resistance on stainless steel. [3, 48; 16, 2-14; 14, 5]

3.2 Alkaline Pickling

Pickling can also be done in strong hot alkaline solution to avoid base metal loss and hydrogen embrittlement. Method is slower than acid pickling and is not commonly used for steel. Hydrogen embrittlement and acid residues can be avoided using alkaline pickling. Using alkaline pickling at higher temperatures can cause caustic embrittlement. [1, 125; 17, 572; 18]

3.3 Electrolytic Pickling

Electrolytic pickling is faster than normal pickling in cleaning oxides. By this method, a cleaner surface can be achieved. Special equipment is needed, and the method is mainly used in continuous pickling lines. [1, 125-126; 3, 50]

3.4 Nonferrous Metal Pickling

Zinc, copper, aluminium and other metals can also be pickled. Different chemicals may need to be chosen for each application since these metals are usually used as alloys. [1, 128-134]

4 Pickling Acids

4.1 Hydrochloric Acid (HCl)

Hydrochloric acid is the most used pickling acid in Europe. Technical grade hydrochloric acid concentration is 33 % and is slightly yellow in colour. Pure acid is colourless. Hydrochloric acid is also known as muriatic acid. Good pickling efficiency can be achieved even at low temperatures. At normal operating temperatures, different concentrations do not have noticeable differences, but at temperatures below 15 °C, higher concentrations have better efficiency as shown in Figure 3. In temperatures over 30 °C excessive amount of hydrogen chloride gas is evaporated and working without special equipment is impossible. In closed systems temperatures as high as 80 °C can be used. Every rise of 10 °C approximately doubles the efficiency. [1, 115-118; 2, 169-170]

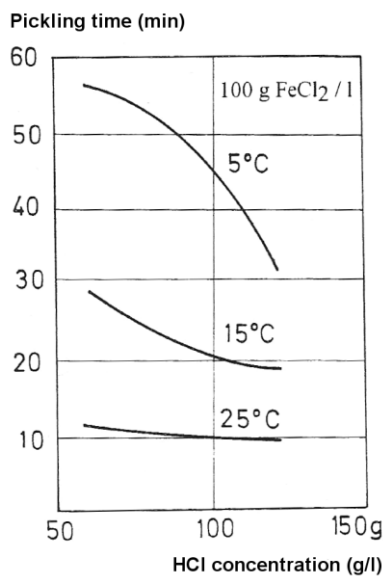


Figure 3. Effect of HCl concentration at different temperatures. [1, 118]

Recommended concentration for pickling is 5–15 %. Inhibitor should always be used when pickling with hydrochloric acid to protect base metal. Hydrochloric acid should not be used with zinc parts or stainless steel. Reaction with zinc is more aggressive than with steel. With stainless steel, chloride ions cause pit corrosion. [1, 115-118; 2, 169-170]

Iron dichloride (FeCl_2) concentration in hydrochloric acid pickling solution has a significant impact on pickling efficiency. Iron dichloride can be added to pickling solution to accelerate reactions as shown in Figure 4. If the saturation point of iron dichloride is reached reactions stop and small green crystals are formed. If this happens, no more acid should be added because more crystals would form. Adding warm water dissolves crystals. [1, 118]

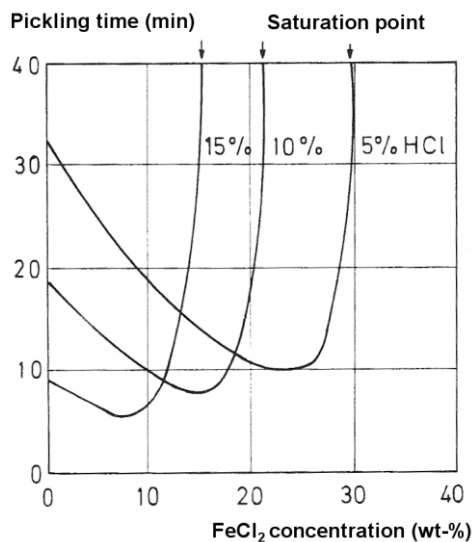


Figure 4. Iron dichloride concentration effect on pickling times at 20 °C. [1, 118]

In the EU regulation 1272/2008 on classification, labelling and packaging of substances and mixture, hydrochloric acid is classified as follows: [19]

- Concentrations $\geq 25\%$
 - Hazard class and category code
 - Skin corrosion 1B
 - Hazard statement code
 - H314 - Causes severe skin burns and eye damage
- Concentration between 10–25 %
 - Skin irritation 2
 - H315 - Causes skin irritation
 - Eye irritation 2
 - H319 - Causes serious eye irritation
- Concentration $\geq 10\%$
 - Specific target organ toxicity - single exposure (3)
 - H335 - May cause respiratory irritation

The transportation class of hydrochloric acid is corrosive (8) and packaging group is II. Special consideration is needed when transporting and storing acids and alkali. [20; 21]

4.2 Citric Acid ($C_6H_8O_7$)

Citric acid is usually sold as anhydrous ($C_6H_8O_7$) or monohydrate ($C_6H_8O_7 \cdot H_2O$) powder. To provide faster pickling times, citric acid is used at temperatures up to 90 °C. No irritating fumes are evaporated even at high temperatures. Additives and agitation can be used to speed the process. Citrates and hydrogen are produced between oxides and metal to remove oxide layer. A concentration between 2–10 % is recommended. [2, 170; 3, 53]

Citric acid is not considered to be a dangerous good in transportation. According to the EU regulation 1272/2008 citric acid causes eye irritation category code 2 and has hazard statement H319 (Causes serious eye irritation). Thus, it is a safe option, but as with all acids heat is released when diluted. [19; 22]

4.3 Phosphoric Acid (H_3PO_4)

Phosphoric acid is an effective oxide remover at concentrations between 15–70 %. It does not attack base metal as aggressively as hydrochloric and sulfuric acid. A low 1–2 % concentration can be used to produce an iron phosphate layer. It protects metal from corrosion and provides a good surface for paint. [1, 124-125; 2, 170]

The transportation class of phosphoric acid is corrosive (8) and packaging group is III. In the EU regulation 1272/2008, phosphoric acid is classified as follows: [19; 23]

- Concentration \geq 25 %
 - Skin corrosion 1B
 - H314 - Causes severe skin burns and eye damage
- Concentration between 10–25 %
 - Skin irritation 2
 - H315 - Causes skin irritation
 - Eye irritation 2
 - H319 - Causes serious eye irritation

4.4 Sulfuric Acid (H₂SO₄)

Sulfuric acid is the most used pickling acid in the USA. Its efficiency is extremely temperature dependant as shown in Figure 5. Excessive amounts of vapours are not evaporated even at high temperatures. Inhibition to protect base metal is recommended. Sulfuric acid is usually sold at concentrations over 90 %. Recommended concentration for pickling is between 5–10 %. [1, 121-124]

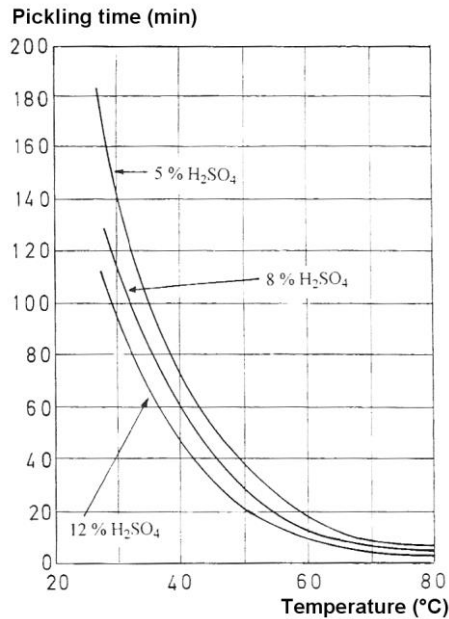


Figure 5. Sulfuric acid efficiency. [3, 122]

The transportation class of sulfuric acid is corrosive (8) and packaging group is II. In the EU regulation 1272/2008, sulfuric acid is classified as follows: [19; 24]

- Concentration ≥ 15 %
 - Skin corrosion 1A
 - H314 - Causes severe skin burns and eye damage
- Concentration between 5–15 %
 - Skin irritation 2
 - H315 - Causes skin irritation
 - Eye irritation 2
 - H319 - Causes serious eye irritation

Extreme caution should be used when diluting sulfuric acid because an extreme amount of heat is produced in the reaction. Concentrated sulfuric acid also absorbs water from air, and open containers can overflow if stored for a long time. [1, 121-124]

4.5 Other Acids and Mixtures

Hydrofluoric acid (HF) can be used to remove mill scale, but it is extremely dangerous if spilled. Nitric acid (HNO₃) attacks steel aggressively, and normal additives do not work with it. Handling and process management of nitric acid need special care. Mixture of hydrofluoric acid and nitric acid is commonly used to clean stainless steel. Hazardous nitrogen oxides are formed when pickled with nitrogen acid. [2, 170; 1, 127; 10, 3]

Formic (HCOOH) and acetic acid (CH₃COOH) and other organic acids are used in mixtures with citric acid or hydrochloric acid. As a single acid, citric acid is more effective, cheaper and safer than formic and acetic acid. [2, 170; 3, 53]

Sulfamic acid (H₃NSO₃) can be used to remove carbonate scales and iron oxide, but it is less effective than hydrochloric acid. Perchloric acid (HClO₄) is mostly used to clean stainless steel. [2, 170]

Mixtures can be used to remove more diverse variety of impurities and to increase efficiency with different alloys. A wide variety of chemicals might be needed to remove complex impurities. [2, 168-170]

4.6 Comparison of Acids

Hydrochloric, citric and phosphoric acid comparison is shown in Table 1. Sulfuric acid was not taken into comparison because according to the literature it is suitable only when heated. Prices are approximate values calculated for making 3000 litres of pickling solutions and neutralizing it with sodium hydroxide. The price effect of additives or transportation is taken into account. Prices were asked from three Finnish companies. The numbers used to calculate the prices are shown in Appendix 3.

Table 1. Comparison of acids. [1, 116-125; 2, 170]

Acid	Hydrochloric	Citric	Phosphoric
Concentration	10 %	6.5 %	20 %
Sold as	33 % solution	powder	85 % solution
Price (see Appendix 3)	662 €	565 €	2004 €
Price ratio compared to citric acid	117 %	100 %	355 %
Temperature	15–30 °C	20–90 °C	20–50 °C
Efficiency when cold	Excellent	Poor	Good
Efficiency when heated	Excellent	Good	Excellent
Pickling inhibition	Needed	Recommended	Not needed
Wetting agent	Recommended	Recommended	Recommended
Corrosion inhibition	Needed	Recommended	Not needed
Hazards	Skin corrosion 1B Specific target organ toxicity - single exposure (3)	Eye irritation 2	Skin corrosion 1B
Hazards during use	Skin irritation 2 Eye irritation 2 Specific target organ toxicity - single exposure (3)	Eye irritation 2	Skin irritation 2 Eye irritation 2
Transport hazard class	Corrosive (8)	Not dangerous	Corrosive (8)
Packaging group	II		III

Citric acid is the cheapest and the safest option for pickling. Hydrochloric acid is only a bit more expensive but needs special attention when transported and used. The advantage with phosphoric acid is that inhibitors are not necessarily needed because an iron phosphate layer is formed in the process. [1, 125]

5 Additional Procedures and Alternatives to Pickling

5.1 Wire Brushing

Wire brushing can be used to remove most of the impurities from the surfaces. Part of the scale remains in the surface roughness. Wire brushing does not cause serious roughening of the surface. Complex parts are hard to clean using wire brushes. Special equipment such as pipeline pigs are available to clean pipes. Brushing can be used to break the oxide layer and that way increase pickling efficiency. [25, 17; 26; 16, 13; 2, 173]

5.2 Abrasive Blasting

Dry abrasive blasting can be used to remove most of the surface oxides, but cleaning effect is not usually as good as with pickling. Different media can be used to produce different surface smoothnesses. Silica sand was broadly used, but the health hazard of dust has limited its usage. Media such as steel grit, cut wire and aluminium oxide grit are options with less dust and good cleaning efficiency. Softer alternatives such as crushed nut shells, glass beads, dry ice and sodium bicarbonate are used to remove softer impurities such as old paint layers and are not used to remove an oxide layer. Round shot style media used to produce smoother or peened surfaces can cause some contaminants to be trapped in the surface as shown in Figure 6 and should not be used to remove an oxide layer. [27; 2, 172; 28]

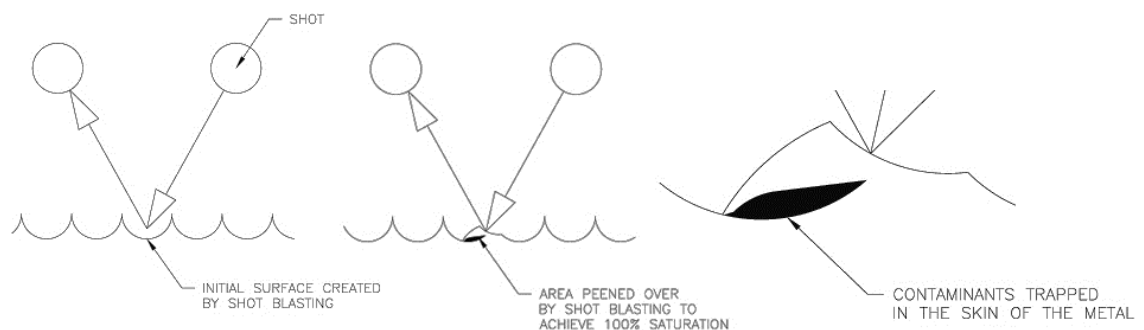


Figure 6. Contaminant trapping mechanism when using shot style blast media. [27]

Abrasive media can be used with water to provide better cleaning efficiency. Water with additives removes grease and salts while blasting media removes oxides. Corrosion

inhibitors can also be used to prevent flash rusting. Wet abrasive blasting requires special equipment and is not commonly used. [29]

5.3 Grinding

Grinding is usually used just to remove welding defects and scratches to provide smoother surfaces. If rough grinding equipment is used, finer equipment should be used afterwards to ensure a smooth surface which is better for corrosion resistance. [15, 7; 16, 12]

5.4 Water Jetting

Ultrahigh-pressure water blasting (220 MPa) is capable of removing scale but not the entire oxide layer. If complete removal of oxide is not necessary, water jetting is fast and environment-friendly. Special equipment that is available only from very few vendors is required. Lower pressures can be used to remove paint and salts. [25, 17; 2, 172-173, 30, 1]

5.5 Thermal Cleaning

Oxygen acetylene torch or oven can be used to remove grease, paint, scale and rust with the help of machine wire brushing. This method is usually used with old greasy parts. Steam can be used to remove scale and debris from surfaces. Oxide is not removed completely using thermal cleaning methods. [25, 17; 2, 173]

6 Corrosion Causes and Prevention in Pickling Applications

6.1 Corrosion

Metals tend to return to the lowest energy state possible by means of corrosion. Metals form oxides to achieve this. Different metals, alloys and grains have different electrode potentials. Galvanic couple is formed between two different potential areas in an electrolyte. Part does not need to be completely immersed because even a moisture layer on a surface can act as electrolyte and cause corrosion. When corrosion advances, potentials can shift, and the entire surface will corrode. The reaction mechanism and reactions are displayed in Figure 7. [15, 4; 17, 17-42]

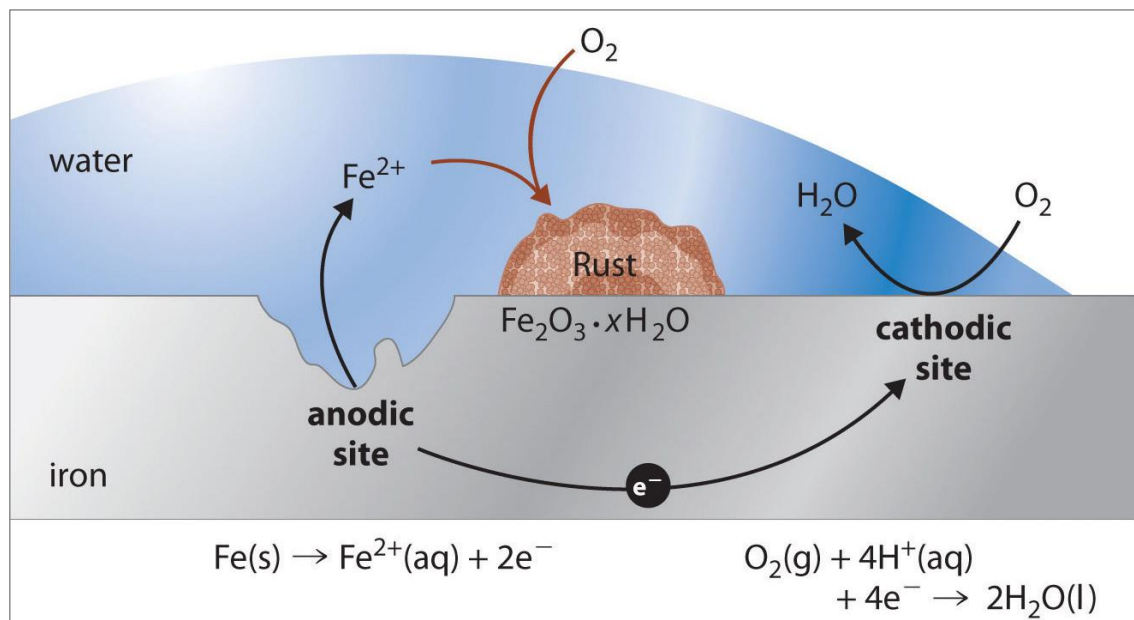


Figure 7. Galvanic corrosion. [31]

6.2 Rinsing, Neutralisation and Drying

Acid residues and dissolved iron stay on the surface after water evaporates. Iron particles tend to turn into rust when oxygen and even a bit of moisture is present. Acid residues, especially hydrochloric acid chlorides, increase the likelihood of corrosion. These residues should be rinsed off, and the surface should be dried rapidly to prevent corrosion. An alkaline solution can be used to neutralize acid residues and to adjust pH to a level where rust is not formed. Corrosion inhibitors can be mixed with acid or

rinsing water to prevent corrosion. The moisture of rinsing water should be removed from the surfaces as fast as possible. Compressed air is effective, and heated rinse water improves drying effect. [12, 92; 32]

6.3 Inhibitors and Alternative Options

Some method to prevent corrosion after pickling and rinsing is usually necessary. An easy way is to apply corrosion inhibitors is to mix them in rinsing water or acid solution. Other temporary ways to prevent corrosion are oils or volatile corrosion inhibitors (VCI) in forms of paper, plastic film or powder. A properly selected and applied corrosion inhibitor can prevent corrosion almost completely. Figure 8 shows an effect of corrosion inhibitor layer application on right. The inhibitor layer has prevented the reaction between metal and oxygen. More information on inhibitors can be found in chapter 2.2.3. [33, 6-8]



Figure 8. Waterborne corrosion inhibitor Cortec VpCI-337 effect. [34]

6.4 Nitrogen Gas

Inert gasses can be used in closed systems to prevent corrosion by displacing oxygen. Nitrogen gas is the most commonly used gas because it can be produced easily from air by using a nitrogen generator. Nitrogen can absorb more moisture than compressed air. If residual moisture is not present on the surfaces, galvanic or microbial corrosion does not happen. Nitrogen is safe to use because it is non-flammable and may be released into the air after use. Carbon dioxide may also be used but some alloys show potential for corrosion with CO₂. [35; 36; 33, 11]

6.5 Magnetite Layer

A protective magnetite layer can be formed on carbon steel to protect the material from corrosion. This method is generally used in boilers. The surface must be in contact with over 100 °C oxygen-free water. The recommended temperature range is 200–240 °C (equivalent pressure 15–35 bar) to provide fast formation so the method can only be used in closed systems. At lower temperatures, ferrous hydroxide (Fe(OH)₂) is formed, and it is transformed to magnetite (Fe₃O₄) when the temperature rises. Rust (FeOOH) is formed if water contains oxygen. [37, 1-3]

7 Tests and Results

7.1 Test Pieces

Welded mild steel tube P235TR1 (EN 10217-1) was chosen for all tests. Appendix 1 shows the exact composition of the tube used. The tube's outside diameter was 60.3 mm and its wall thickness was 2.9 mm. A pipe of 3 m was cut in 44-mm pieces with a circular metal saw to get approximately 180 g pieces. Numbers were punched to pieces for identification. Sharp edges were rounded off. A picture of the piece is shown in Figure 9. The chosen size fitted in a 400 ml low form glass beaker and in the analytical balance. Test pieces were cleaned first with a detergent and then with a 5 % sodium hydroxide at 60 °C for 3 minutes. After cleaning, pieces were rinsed thoroughly in warm tap water and dried with compressed air.



Figure 9. Test piece.

7.2 Test Chemicals

Best acids for mild steels were chosen based on the literature emphasizing ease of use and efficiency in cold temperatures. Temperatures were chosen to represent situations where heating is limited or not used. Overlapping temperature ranges were used with each acid to provide comparable data between the chemicals. Main concentrations were chosen to present common values found from the literature. Additional concentrations were chosen to represent minimal and maximum values occurring in the

literature. Parameters were chosen to represent possible previously used and easy to use values when process measurement and control systems are limited.

Suitable time for tests was determined by following first pickling in 6.5 % citric acid for an hour at 50 °C. Pieces were clean at the end of the preliminary test so 15 minutes was chosen for the following tests. After tests the pieces were rinsed with tap water at 50 °C thoroughly and then blown dry with compressed air.

7.3 Citric Acid Weight Loss at Different Temperatures

Citric acid was tested with 3.5 %, 6.5 % and 9.5 % concentrations. The 6.5 % concentration was tested at ten-degree intervals between 10 °C and 60 °C. The 3.5 % and 9.5 % concentrations were tested at 30 °C and 50 °C. Approximately 1 ml/l of ethanol was added to lower surface tension. No inhibitor was used.

The efficiency of citric acid showed a clear increase when the temperature rose. Higher concentrations had better efficiency, but the differences between tested concentrations stayed relatively small as shown in Figure 10.

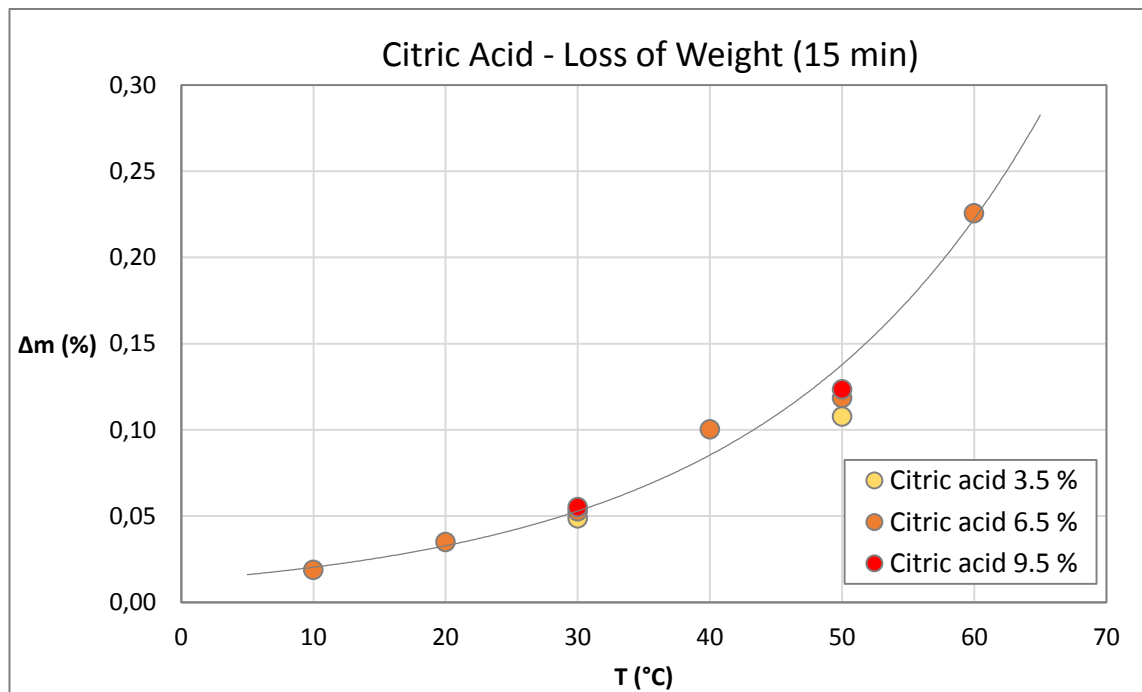


Figure 10. Citric acid weight loss over temperature.

Higher temperatures and a wider range of concentrations could be tested to provide a better overview of pickling. The effect of additives and agitation could be tested to see the potential of citric acid.

7.4 Citric Acid Pickling Inhibitor Comparison

Test pieces were first pickled clean in 10 % HCl for 3 h at 25 °C. The pieces were rinsed and dried quickly to prevent any oxide layer formation. Then the pieces were placed in 6.5 % citric acid with different inhibitors for 20 h to compare inhibitor efficiencies.

Formalin with 10–15 % methanol (10 %), Rhodia Stannine LTP (0.1 %), succinic acid (0.2 %) and eucalyptus globulus oil (0.5 %) were used as inhibitors. Formalin and Rhodia Stannine LTP were chosen because they had been used for inhibition in these kinds of circumstances previously, and succinic acid and eucalyptus oil were chosen to represent more environment friendly options based on research. The same inhibitors were used also with hydrochloric acid. The piece was also pickled in a non-inhibited solution. The pieces were weighed and inhibitor efficiencies were calculated using Equation (1) and are shown in Figure 11. This equation is commonly used when comparing inhibitor efficiencies. W_0 is weight loss of uninhibited piece, and W_i is weight loss of inhibited piece. Weight loss values are shown in Appendix 2. [8]

$$(\%) = \frac{W_0 - W_i}{W_0} \times 100 \quad (1)$$

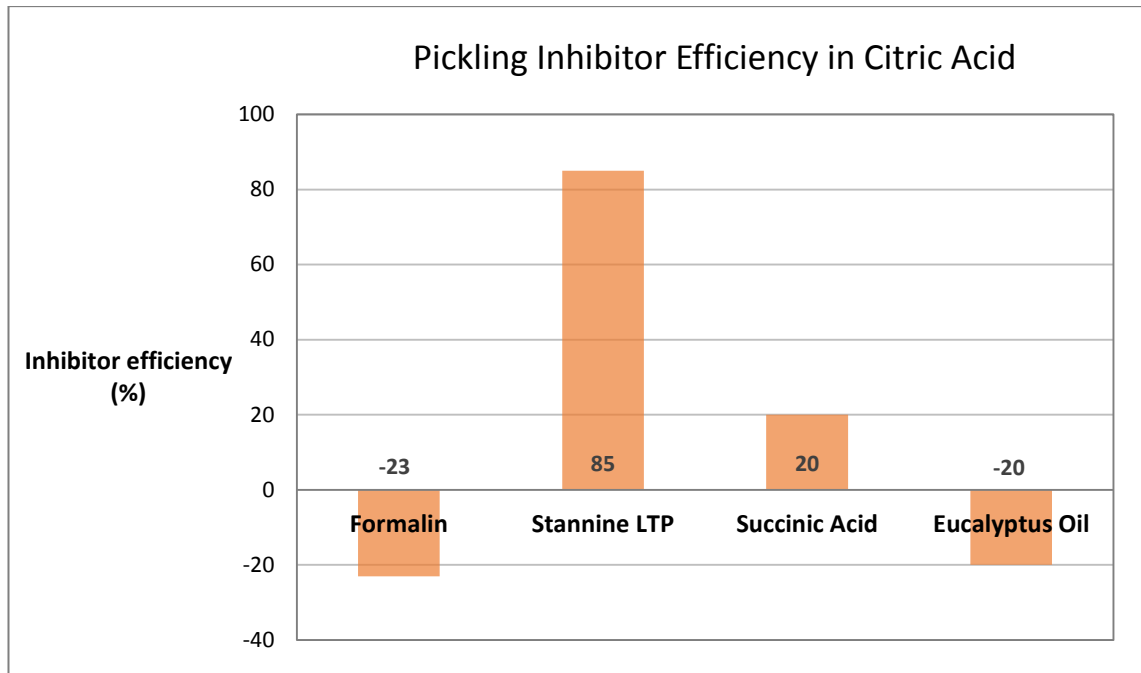


Figure 11. Citric acid inhibitor comparison.

Stannine LTP performed as expected. It is designed to be used in pickling with all normal acids except hot hydrochloric acid. Formalin efficiency was surprising because it sped up the corrosion. Formalin is used in inhibitors for hydrochloric acid, but other data is very limited. Overall weight loss was surprisingly high. Uninhibited weight loss was higher than in uninhibited hydrochloric acid. Inhibitors could be tested at different temperatures to provide data if inhibition efficiency is lost at higher temperatures. Results show that succinic acid can be used to protect base metal a bit, whereas eucalyptus oil speeds up base metal corrosion and should not be used for inhibition. Eucalyptus oil and formalin stabilized with methanol probably affected surface tension and that way increased the corrosion rate.

7.5 Citric Acid Weight Loss over Time

The test piece was pickled in 6.5 % citric acid at 20 °C for 9 hours to see if weight loss increase is irregular. The piece was weighed before the test, after 30 minutes from the start and every hour. No inhibitor or additives were used.

Figure 12 shows slight reduction in weight loss after the oxide layer was removed. The test piece was visually clean from oxides after 6 h when a little under 600 mg was

removed. After that, the graph shows some decrease after oxide has been removed. The test could be continued and surface analysis be performed to understand better if the inhibitor should unambiguously be used with citric acid. The test could be performed also with different acids.

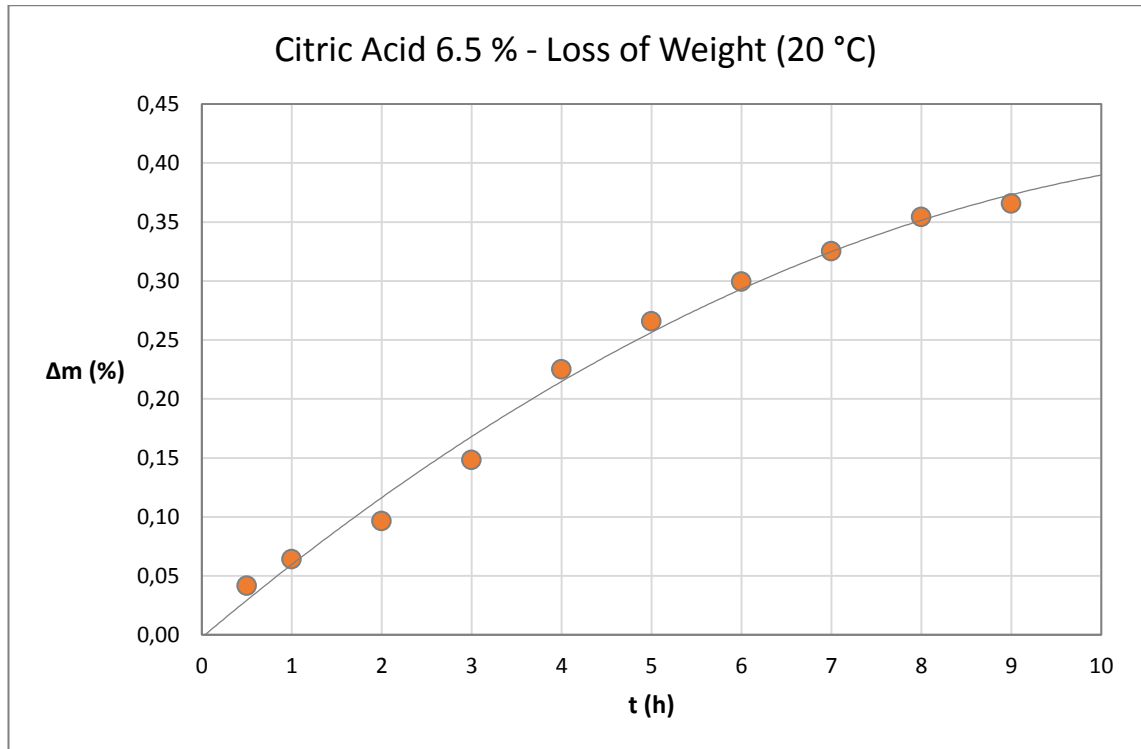


Figure 12. Weight loss progress in citric acid.

7.6 Hydrochloric Acid Weight Loss at Different Temperatures

Hydrochloric acid was tested with approximately 3.7 % formaldehyde inhibitor (10 % formalin) to protect the base metal from corrosion. Formalin contained also 10–15 % methanol as stabilizer. The tested concentrations were 7.5 %, 10 % and 12.5 %. Temperatures were 10 °C, 20 °C and 30 °C to see low temperature efficiency and to keep the working conditions safe. Hydrochloric acid pickled pieces were neutralized in 10 % NaOH to prevent rusting after tests.

Hydrochloric acid performed well at all temperatures and concentrations as shown in Figure 13. Low concentration and low temperature showed reduction in efficiency. Differences between selected concentrations were small.

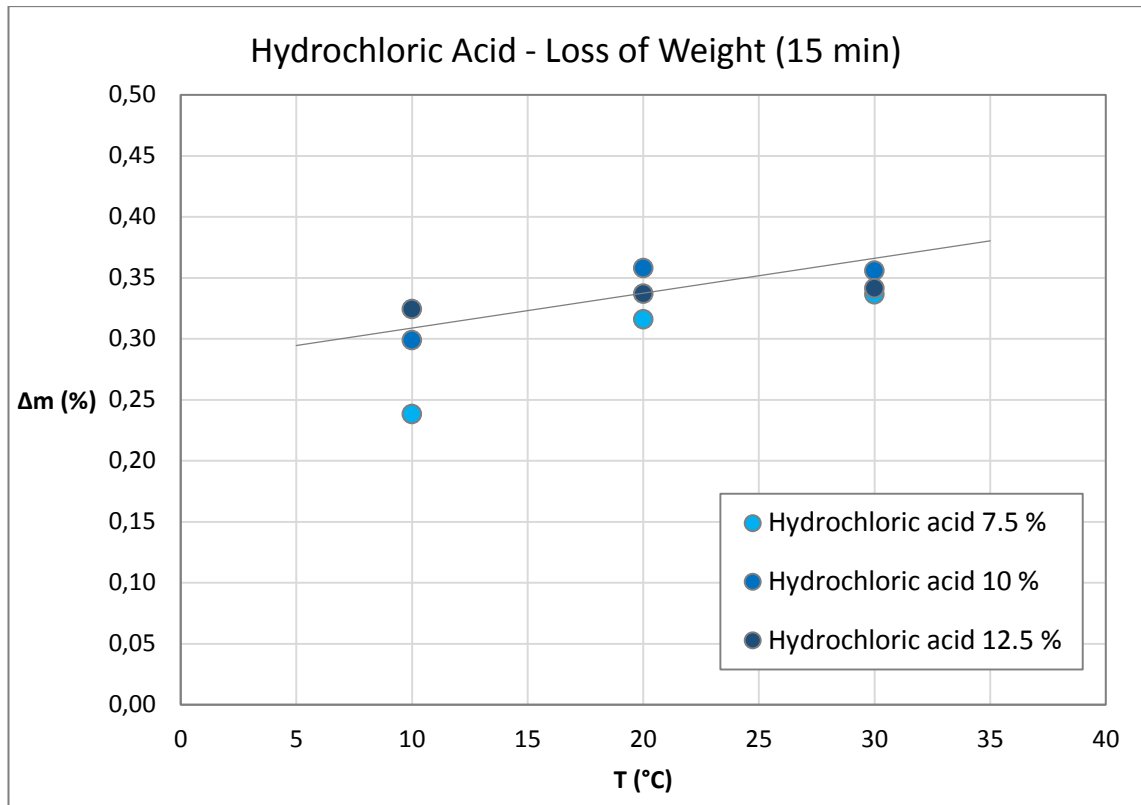


Figure 13. Hydrochloric acid weight losses over temperature.

Data on lower and higher concentrations and different FeCl concentrations are available so a comparison of additives could be made to provide new information. Agitation usefulness could be also tested.

7.7 Hydrochloric Acid Pickling Inhibitor Comparison

Test pieces were first pickled clean in 10 % HCl for 3 h at 25 °C. The pieces were rinsed and dried quickly to prevent any oxide layer formation. Then the pieces were pickled in 10 % HCl with different inhibitors for 20 h to compare inhibitor efficiencies.

Formalin with 10–15 % methanol (10 %), Stannine LTP (0.1 %), succinic acid (0.2 %) and eucalyptus globulus oil (0.5 %) were used as inhibitors. The piece was also pickled in non-inhibited solution. As with citric acid, the pieces were weighed, and inhibitor efficiencies were calculated using Equation 1. Results are shown in Figure 14.

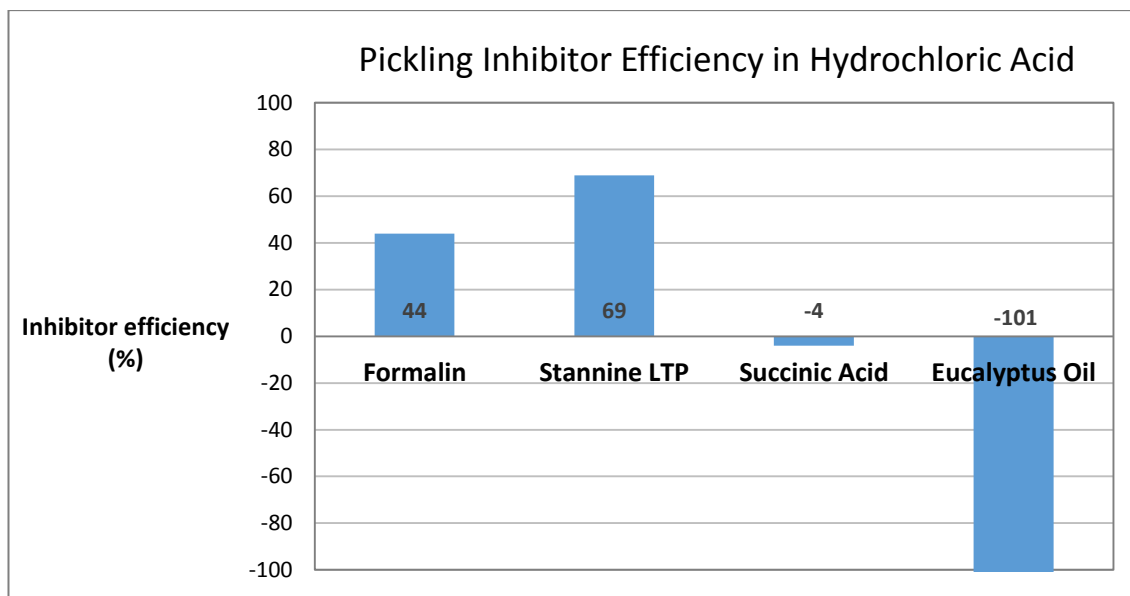


Figure 14. Hydrochloric acid inhibitor comparison.

Stannine LTP worked well, but formalin did not perform as well as expected. Formaldehyde is a common ingredient in commercial inhibitors, but they also contain other chemicals. The result for eucalyptus oil was also unexpected. It seems that it only worked as a wetting agent. Eucalyptus oil and succinic acid were expected to work because there are studies showing they work in weak hydrochloric acid. FeCl addition could be tested to see if efficiency is different through the whole pickling process. Other inhibitors recommended for HCl could be tested to provide understanding if efficiencies are as good as manufacturers claim them to be.

7.8 Phosphoric Acid Weight Loss at Different Temperatures

Phosphoric acid concentrations were 10 %, 35 % and 75 % to see if there is a difference between iron phosphate formation and detachment. Temperatures for the 35 % concentration were at ten-degree intervals between 20 °C and 50 °C. 10 % and 75 % concentrations were tested at 20 °C and 40 °C. No inhibitor or additives were used.

The temperature affected cleaning efficiency explicitly as shown in Figure 15. The highest concentration was viscous at a low temperature. Poor wetting probably caused reduction in efficiency. At a higher temperature the difference between viscosities was invisible. A lower concentration also reduced efficiency. No visual differences after pickling were detected between concentrations.

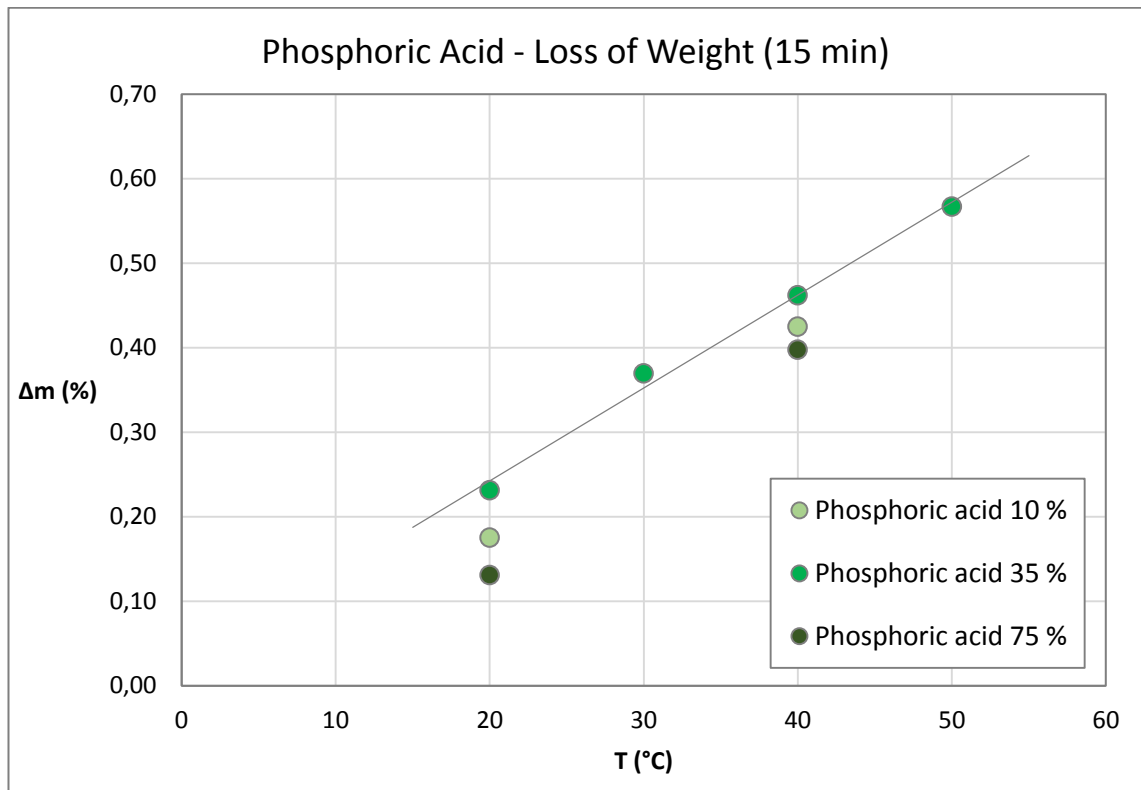


Figure 15. Phosphoric acid weight losses over temperature.

Wetting agent addition, inhibitor addition and concentrations between 5–35 % could be tested to provide an optimal recipe for pickling mild steel. A surface analysis could be made to detect the iron phosphate layer. Corrosion tests could be run to see corrosion protection differences.

7.9 Effect of Rinse Water Temperature on Acid Residues

Determination of residual acid on the pickled surface was tried after rinsing the pieces in water at different temperatures. The test pieces were pickled for 30 minutes in 6.5 % citric acid at 70 °C and 10 % hydrochloric acid at 20 °C. After the pickling, the test pieces were roughly dried with compressed air and then placed in 800 ml of deionized water at 15, 45 and 70 °C. After 5 minutes without agitation, the pieces were roughly dried again with compressed air and then placed in 400 ml of deionized water at 50 °C with magnetic stirrer for 20 minutes. The pieces were removed from the beakers.

Three drops of phenolphthalein were added to the beakers. The solution was titrated with 0.01 mol/l NaOH to show the amount of residual acid. Also two samples of deionized water were titrated to see what the NaOH consumption without acid residue was.

After examining the first batch, one piece was tested with a shorter rinsing time. The test piece pickled with hydrochloric acid was kept in 15 °C water for 1 minute and then rinsed again for a longer period of time in 60 °C water with a magnetic stirrer.

Deionized water results were 4.2 ml and 8.2 ml. The NaOH consumption results for acid residues are shown in Table 2. NaOH consumption for the sample with a short 1-minute rinsing time was 5.3 ml.

Table 2. Results of acid residue titration.

	15 °C	45 °C	70 °C
Citric acid	4.9 ml	10.5 ml	7.1 ml
Hydrochloric acid	4.5 ml	4.1 ml	5.6 ml

Results were inconsistent. No connection between the rinse water temperature and the acid residue can be made based on this test. Residue amount measurements should be made using a different method. Acid residues could be measured without compressed air using multiple rinsing baths and measuring acid concentration of the last bath.

7.10 Summary

Figure 16 shows weight loss results. The measurement table of tested weight losses is shown in Appendix 2.

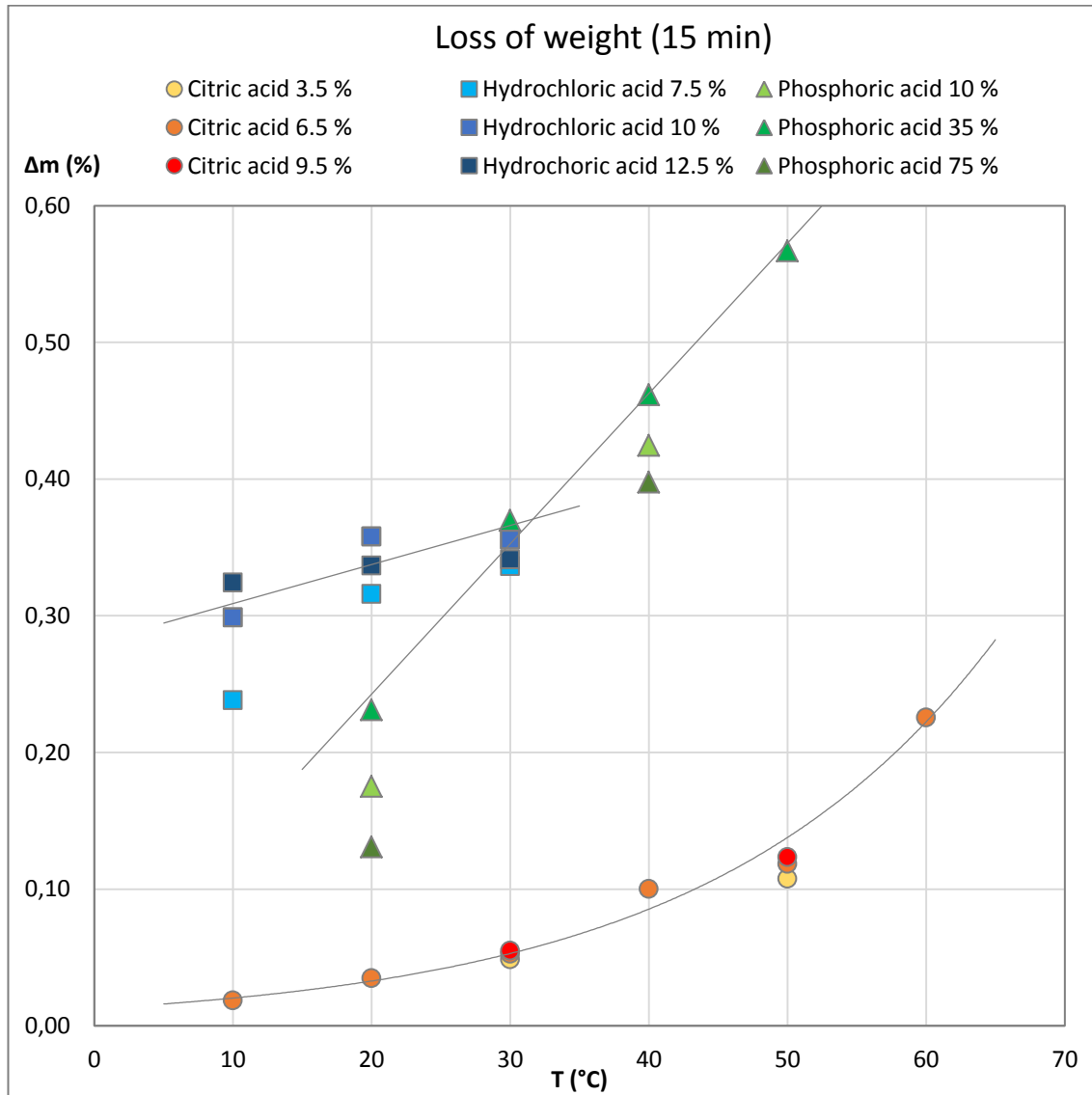


Figure 16. Citric acid weight loss over temperature.

The graphs in Figure 16 show that hydrochloric and phosphoric acid are more efficient at lower temperatures than citric acid. Citric acid should be used with some heating to provide reasonable pickling times. In circumstances where equipment is limited and safety raises concerns, citric acid is an excellent option.

8 Conclusions and Recommendations

On the basis of information collected and tests made, citric acid seems to be a good option for pickling steel in conditions where equipment is limited. If the citric acid solution can be heated above 60 °C, the efficiency is equal to that of hydrochloric acid. At lower temperatures citric acid requires more time compared to hydrochloric or phosphoric acid, but it is the best option from the price, transportation and safety perspective. It is also easily available as it is used in the food industry and other industrial sectors.

Literature and tests showed that acid consumption and base metal loss is greatly reduced even with a minimal amount of inhibition and could be recommended for all acids. Because commercial inhibitor products usually contain also wetting agents, iron oxide is removed faster, or alternatively, lower temperatures can be used to achieve same efficiency. The advantages of using inhibition during pickling is clear, but chemicals should be selected on a case-by-case basis in order to provide proper action.

Pickling is usually the best option if complex parts such as tubes and machined parts need to be cleaned. For instance, the special nozzles needed with blasting and high pressure water cleaning are expensive and might not be sufficient to provide results as good as those given by pickling. In addition, pickling produces even surface quality, and there is no risk of contamination from the blast media. Depending on the application, the required surface quality may also be impossible to achieve with abrasive blasting, wire brushing and water cleaning. Alternative methods can be more cost-effective when used for cleaning simple products such as sheets and wires in continuous cleaning lines.

Weight loss tests worked as expected and provided good data on acids. Inhibitor tests were successful and showed the importance of properly selected inhibitor. Data on the effect of the rinse water temperature on acid residues would have been helpful in order to avoid unnecessary heating. Further research should be focused on inhibition and acid residues to provide more optimal cleaning process. Also more acids, a wider temperature range and the effects of additives on efficiency could be tested to provide recommendations for different conditions.

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Test Material Inspection Certificate

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Tel. +39 0372 4091
Fax +39 0372 413170

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Number	282298	date	11/04/2013
Our order	0211153702	/	40
Customer order	4500123918		
date	10/04/2013		
Consegna	0221192380		
delivery	0000208048	date	11/04/2013

Messrs	ONNINEN OY
P.O. BOX 109	
01301 VANTAA	
	FI

Description **TUBE FIN CUT**

Standard **EN 10217-1 TR1 BOL**

Steel grade **P235TR1**

Dimensions **BOL 60,3x2,9x6000 ERW EN 10217-1 TR1**

Tubes **357 MT 2.142,00 KG 8.940,00**

Chemical analysis

	C	Mn	Si	P	S	Al	Cr	Ni	Mo	Cu	Sn	V	Nb	Ti	B	N	
min						0,0200											
max	0,1600	1,2000	0,3500	0,0300	0,0250		0,3000	0,3000	0,0800	0,3000		0,0200	0,0100	0,0400			
3036334A	0,0319	0,1034	0,0237	0,0084	0,0014	0,0247	0,0406	0,0557	0,0106	0,1547		0,0020	0,0014	0,0010			
3037040A	0,0297	0,4500	0,0240	0,0060	0,0017	0,0254	0,0328	0,0704	0,0139	0,1576		0,0022	0,0014	0,0010			
3036334A	CR+CU+MO+NI								<=0,7		0,26						
3037040A	CR+CU+MO+NI								<=0,7		0,27						

Mechanical and technological tests

Works Nr.	Heat	Lot	Tubes	R (MPa)		REH (MPa)	A(%)	Rs/R	Fm (N)
				>= 360	<= 500	>= 235	>= 25,0		
1 3036334	3036334A			389		309	35,00		
2 3037040	3037040A			421		309	38,00		

Test	Standard	Required	Result
Non destructive test	EN 10246-3	%	100 POSITIVE
Dimensional inspection	EN 10217-1	LOT	1 POSITIVE
Flattening test	EN ISO 8492	MM	2 POSITIVE
Leak tightness test	EN 10246-1	%	100 POSITIVE
Visual	EN 10217-1	%	100 POSITIVE

Remarks



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e-mail: controllo.qualita@ata.arvedi.it

We hereby certify, that the material described above has been tested and complies with the terms of the order contract. This certificate has been created by a data processing system and does not contain a personal signature but the name and the official address of the appointed department.



Germanischer Lloyd
WZ 944 HH 2



Measurement Table

#	Test	Acid	Concentration (wt%)	Temperature (°C)	Time (min)	Original weight (g)	Weight after (g)	Loss of weight (g)
0	Difference test 1 - Most corroded	Citric	6.5	50	60	183.0262	182.1682	0.8580
47	Difference test 1 - Least corroded	Citric	6.5	50	60	186.0737	185.2879	0.7858
3	Difference test 2	Citric	6.5	60	240	184.7758	183.1920	1.5838
12	Difference test 2	Citric	6.5	60	240	185.9032	184.3403	1.5629
20	Difference test 2	Citric	6.5	60	240	183.4275	181.9561	1.4714
27	Difference test 2	Citric	6.5	60	240	187.0328	185.4413	1.5915
36	Difference test 2	Citric	6.5	60	240	185.5852	184.0133	1.5719
48	Difference test 2	Citric	6.5	60	240	189.0820	187.4420	1.6400
1	Inhibitor test - No inhibitor	Citric	6.5	20	1200	182.7495	182.6067	0.1428
4	Inhibitor test - Formalin 10 %	Citric	6.5	20	1200	183.7710	183.5954	0.1756
11	Inhibitor test - Stannine LTP 0.1 %	Citric	6.5	20	1200	184.1264	184.1048	0.0216
15	Inhibitor test - Succinic acid 0.2 %	Citric	6.5	20	1200	185.0695	184.9557	0.1138
16	Inhibitor test - Eucalyptus oil 0.5 %	Citric	6.5	20	1200	185.9189	185.7477	0.1712
41	Loss of weight over time	Citric	6.5	20	30	185.6682	185.5906	0.0776
41	Loss of weight over time	Citric	6.5	20	60	185.6682	185.5486	0.1196
41	Loss of weight over time	Citric	6.5	20	120	185.6682	185.4891	0.1791
41	Loss of weight over time	Citric	6.5	20	180	185.6682	185.3924	0.2758
41	Loss of weight over time	Citric	6.5	20	240	185.6682	185.2502	0.4180
41	Loss of weight over time	Citric	6.5	20	300	185.6682	185.1745	0.4937
41	Loss of weight over time	Citric	6.5	20	360	185.6682	185.1121	0.5561
41	Loss of weight over time	Citric	6.5	20	420	185.6682	185.0641	0.6041
41	Loss of weight over time	Citric	6.5	20	480	185.6682	185.0104	0.6578
41	Loss of weight over time	Citric	6.5	20	540	185.6682	184.9889	0.6793
24	Weight loss	Citric	3.5	30	15	185.2972	185.2069	0.0903
22	Weight loss	Citric	3.5	50	15	184.0225	183.8223	0.2002
25	Weight loss	Citric	6.5	10	15	184.8644	184.8296	0.0348
17	Weight loss	Citric	6.5	20	15	184.4831	184.4183	0.0648
49	Weight loss	Citric	6.5	30	15	186.0810	185.9831	0.0979
2	Weight loss	Citric	6.5	40	15	184.9923	184.8062	0.1861
23	Weight loss	Citric	6.5	50	15	184.7183	184.4982	0.2201
19	Weight loss	Citric	6.5	60	15	184.3746	183.9555	0.4191
10	Weight loss	Citric	9.5	30	15	184.5943	184.4920	0.1023
34	Weight loss	Citric	9.5	50	15	186.4490	186.2197	0.2293
18	Inhibitor test - No inhibitor	Hydrochloric	10.0	20	1200	184.8769	184.7913	0.0856
22	Inhibitor test - Formalin 10 %	Hydrochloric	10.0	20	1200	183.3055	183.2573	0.0482
29	Inhibitor test - Stannine LTP 0.1 %	Hydrochloric	10.0	20	1200	184.5249	184.4987	0.0262
30	Inhibitor test - Succinic acid 0.2 %	Hydrochloric	10.0	20	1200	186.6461	186.5570	0.0891
31	Inhibitor test - Eucalyptus oil 0.5 %	Hydrochloric	10.0	20	1200	187.6125	187.4402	0.1723
45	Weight loss	Hydrochloric	7.5	10	15	185.8083	185.3656	0.4427
21	Weight loss	Hydrochloric	7.5	20	15	185.0836	184.4965	0.5871
5	Weight loss	Hydrochloric	7.5	30	15	184.7109	184.0859	0.6250
51	Weight loss	Hydrochloric	10.0	10	15	184.9673	184.4123	0.5550
26	Weight loss	Hydrochloric	10.0	20	15	186.9950	186.3301	0.6649
8	Weight loss	Hydrochloric	10.0	30	15	185.9345	185.2734	0.6611
52	Weight loss	Hydrochloric	12.5	10	15	187.7406	187.0961	0.6445
35	Weight loss - Retest	Hydrochloric	12.5	10	15	185.4892	184.9286	0.5606
32	Weight loss	Hydrochloric	12.5	20	15	185.2635	184.6343	0.6292
38	Weight loss - Retest	Hydrochloric	12.5	20	15	188.9190	188.2967	0.6223
9	Weight loss	Hydrochloric	12.5	30	15	185.7378	185.1154	0.6224
50	Weight loss - Retest	Hydrochloric	12.5	30	15	186.9813	186.3355	0.6458
28	Weight loss	Phosphoric	10.0	20	15	185.7601	185.4345	0.3256
6	Weight loss	Phosphoric	10.0	40	15	184.6096	183.8207	0.7889
31	Weight loss	Phosphoric	35.0	20	15	188.4852	188.0557	0.4295
39	Weight loss	Phosphoric	35.0	30	15	186.5323	185.8455	0.6868
13	Weight loss	Phosphoric	35.0	40	15	186.7243	185.8664	0.8579
43	Weight loss	Phosphoric	35.0	50	15	185.8272	184.7738	1.0534
42	Weight loss	Phosphoric	75.0	20	15	186.4673	186.2241	0.2432
7	Weight loss	Phosphoric	75.0	40	15	186.5558	185.8169	0.7389

Prices of Different Acids

Acid	Citric	Hydrochloric	Phosphoric
Concentration (wt%)	6.5	10	20
Amount (l)	3000		
Density (kg/l)	1.025	1.046	1.111
Commercial concentration (wt%)	91	33	85
Amount (kg)	219	951	784
Acid Price (€/kg)	2.005	0.328	1.498
Acid Price (€)	438	312	1174
NaOH amount to neutralize (kg)	125	344	816
NaOH price (€/kg)	1.02		
NaOH Price (€)	127	350	830
Total Price (€)	565	662	2004
Price Comparison to Citric (%)	100	117	355