The quality of hydrochloric acid produced according to technological routes, contaminants and industrial applications

https://doi.org/10.56238/sevened2024.004-007

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ABSTRACT

Hydrochloric acid (HCl), the object of this work, was chosen due to the fact that it has several industrial routes and its use, directly or indirectly, allows contamination in final products. The main industrial processes, the raw materials related to each process, the main contaminants and their consequences were highlighted. To prove some contaminations, experiments were carried out in order to demonstrate that contaminants present in hydrochloric acid can affect the quality and performance of a process where their participation is paramount. Finally, the objective of this work is to form a critical technical awareness to evaluate and use hydrochloric acid for purposes compatible with its industrial quality.

Keywords: Hydrochloric acid, Contaminants, Organochlorines, Industrial processes.

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INTRODUCTION

According to Salager *et al.* [1], although the concept of formulations is still used, it is a fact that obtaining chemical and metallurgical products cannot be considered as a modern concept, as it is directly related to the advancement of ancient civilizations, such as the Roman Empire, in which various utensils of lead, copper and bronze (copper and tin alloys) were manufactured in primitive casting, quite common at that time [2]. The formulations were also employed in the paints used in fresco paintings, in the fermentation of wines, in the processing of olive oils, and in the treatment of leather.

At the end of the eighteenth century, when Alchemy became the Science called Chemistry, as well as from the development of the principles of Electrochemistry and Organic Chemistry in the following century, the second period of the development of formulations began. This enabled the emergence and production of new chemical substances and, consequently, new combinations or formulations. However, at that time research and development were still carried out through experiments based on trial and error [1].

Between 1856 and 1880, Organic Chemistry and the textile industry evolved considerably, and dyes of plant and animal origin were replaced by products synthesized in the laboratory. It is essential to show that this fact resulted in the development of theories and procedures, giving rise to thousands of new molecules, which were used in various industrial segments.

Finally, the third period in the history of formulations began in the 1950s after the Second World War, when there was the junction, integration and interdisciplinarity of the knowledge of the various sciences already consolidated. From this interaction, which ranged from biotechnology to nuclear energy, from toxicity to sustainability, new products were created and developed on an exponential scale, whose advantages and disadvantages currently stand out [1].

Today, it is practically impossible to determine the number of substances and/or chemical formulations present in the various products available to people, such as: disinfectants, paints, personal hygiene products, perfumes, alcoholic and non-alcoholic beverages, pesticides, pharmaceuticals, fertilizers, additives, plastics, rubbers, aerosols, solvents, greases, lubricating oils, metallic or non-metallic alloys, batteries, etc.

Environmental and public health agencies estimate that there are currently more than 800,000 formulations that originate, directly or indirectly, from plants, animals, or synthesized. Also to be considered is the great advance in chemical process technologies, which annually launch more than 8,000 new chemical formulations on the market. Often, several of these products have not been analyzed with a view to compromising the quality of life of the man himself. It is observed that many companies do not pass on to society the degree of quality of their products.

Currently, there are more than 10,000 drug formulations available on the market for doctors to prescribe and for patients to use. The environmental pollution caused by these pharmaceutical formulations and their transformation products has become a growing concern in environmental changes regarding the potential toxic effects on human health. Environmental risk assessments are primarily based on one active component, which causes different ecotoxicological effects, although the specific component is present in the environment as part of a mixture of different pharmaceuticals and excipients [3, 4].

The International Free Market is very large and the low price of products dominates and sabotages quality. Rich countries create obstacles, norms and procedures, while poor countries are left adrift and without a clear direction. The power of industrial civilization is advancing rapidly, imposing its guidelines on commercial and industrial transactions.

Figure 1 shows an example of products sold over the *internet* in the International Free Market, where, for example, sodium nitrite ($NaNO_3$) can be used in various food products [5, 6], as well as as a corrosion inhibitor [7]. The toxic contaminants present in this substance can compromise the lives of human beings, but on the other hand, it does not pose a danger to the integrity of the equipment to be protected.

Figure 1 - Examples of commercial sodium nitrite found in the International Free Market (*internet*)

In the area of chemical processes, the obtaining of substances that may be used directly or indirectly, as chemical intermediates, must meet a series of fundamental factors, such as: origin of raw materials, preservation of the environment, efficiency of equipment and materials, control and monitoring, automation, costs, internal and external market, types of packaging used, competitions, patents, contaminants, etc.

In the case of contaminants, there is an important factor to consider, as it is not always possible to identify or visualize, throughout the industrial process, the problems that may be caused by accidental contamination or contaminants already present in the raw material or originating from the manufacturing processes. In other words, a simple standardized analysis is not always able to identify the contaminants present, especially if they are toxic.

Going back to the past to exemplify the study of hydrochloric acid, it can be seen that one of the industrial objectives of the late eighteenth century was the production of the barrel (sodium carbonate, Na_2CO_3) for the manufacture of soap, glass etc. The first industrial process was developed by Leblanc in 1791 and was based on the reactions:

$$2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl$$

$$Na_2SO_4 + CaCO_3 + 2\ C \rightarrow Na_2CO_3 + CaS + 2\ CO_2 \quad (1000\ ^\circ C)$$

The first soda ash was installed in France in 1792 and all the hydrogen chloride (HCl) produced was released into the atmosphere, creating a major environmental problem at the time. Based on the stoichiometry of the reaction, it can be seen that for one ton of sodium carbonate produced, 688 kg of hydrogen chloride were released into the environment [8].

In England, it was only around 1823 that this gaseous by-product began to be marketed in the form of aqueous solutions (dilute hydrochloric acid) and, probably, production increased due to the enactment of a law prohibiting the release of HCl into the atmosphere. In 1823, the limit for the release of HCl (g) into the atmosphere was set at 5%. It was considered the first pioneering legislation on air pollution. The disposal problem was partially solved, at that time, on the basis of three solutions:

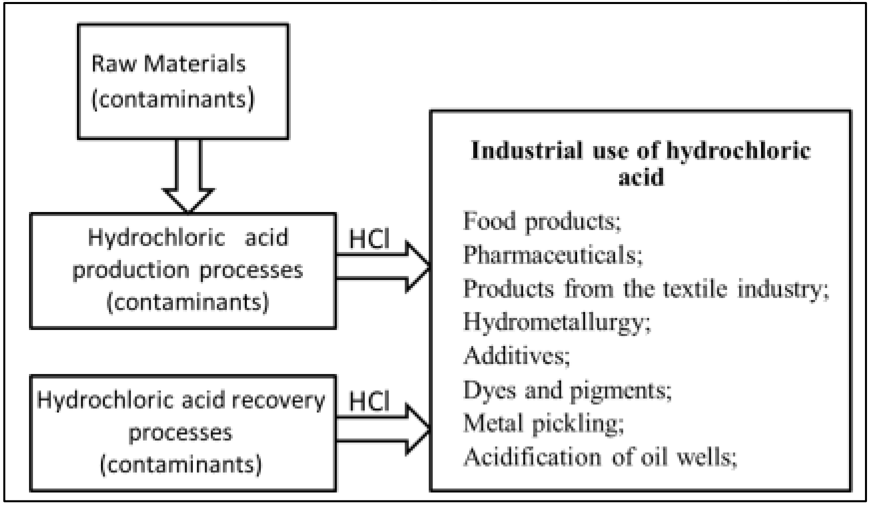
- Use of chimneys of about 30-40 m for dispersion of polluting gases.
- Absorption towers with water for HCl production.
- Chlorine production from burning HCl (g) with air, based on the reaction:

$$4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2\ H_2O$$

Later, this prohibition was set at 0.03% of HCl in the air stream, requiring the use of the HCl produced. All this effort has led hydrochloric acid manufacturers to look for new processes, new markets and new applications.

To highlight the problems arising from these premises, hydrochloric acid was chosen, as shown in Figure 2, because it is a substance used, directly or indirectly, in various industrial processes, such as: in the petroleum industry, in petrochemicals, in food manufacturing, in hydrometallurgy of various ores, in the pharmaceutical industry, etc. In addition, the contaminants present in the raw material, in the production of hydrochloric acid and in its recovery processes are also highlighted.

Figure 2 - Simplified flowchart of contaminants in the production and industrial recovery of hydrochloric acid



Thus, the present study is divided into the following parts:

- Description of the industrial processes for obtaining hydrochloric acid and its main contaminants.
- Analysis of contaminants from hydrochloric acid production processes.
- Use of hydrochloric acid to obtain other chemicals.
- Examples of experiments that show the influence of some contaminants.
- Conclusions.

DESCRIPTION OF THE INDUSTRIAL PROCESSES FOR OBTAINING HYDROCHLORIC ACID AND ITS MAIN CONTAMINANTS

SALT-ACID PROCESS

Conventional salt-acid process

As already reported, this is one of the oldest industrial processes for the production of hydrochloric acid, and in the past it was aimed at the manufacture of sodium sulfate (Na_2SO_4), called Glauber's Salt [9].

The salt used for industrial purposes comes from solar evaporation of seawater or the mining of rock salt. Rock salt can be removed by two methods. The first using procedures similar to coal mining; As the salt is mechanically removed, tunnels are formed supported by columns of the salt itself. The other method of production consists of drilling wells up to the salt dome and, by means of a chosen well, hot water is injected, in such a way that the brine is continuously removed from other producing wells [10-13].

The purity of the salt obtained by evaporation is in the order of 98 to 99%. The cations and anions present are: Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, K^{+}, Fe^{2+}, Cu^{2+}, SO_4^{2-}, F^{-}, Br^{-}, I^{-}, SiO_3^{2-}, CO_3^{2-}, HCO_3^{-}, BO_3^{3-}, depending on the location and charge releases.

In this process, the reaction of sodium chloride with sulfuric acid takes place in two steps:

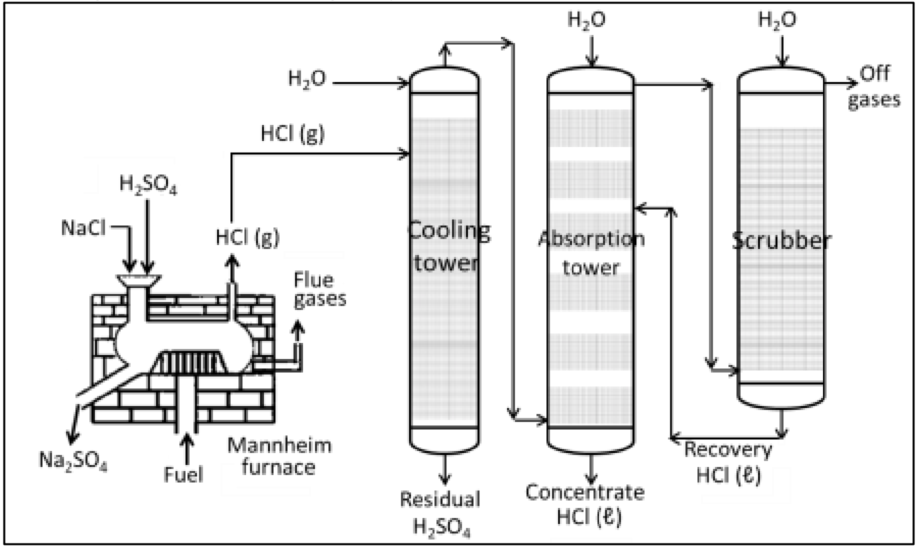
$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$$

The reactions are endothermic, with the first reaction taking place at a temperature of 150°C and the other in the range of 550 to 600°C. Sulfuric acid and sodium chloride are heated in a furnace to form sodium sulfate and hydrogen chloride. Hydrogen chloride contaminated by sulfuric acid droplets and sodium sulfate particles and air pass through coolers, scrubbers and finally is absorbed in absorption towers with water to then form a hydrochloric acid solution as shown in the simplified flowchart in Figure 3.

The furnaces used are of the Mannheim type, consisting of a furnace made of cast iron or iron-silicon alloy, consisting of two plate-shaped parts, one at the top and the other at the bottom, equipped by a melting system in such a way that the molten sodium sulphate is discharged continuously, to measure, that gaseous hydrogen chloride is expelled.

Figure 3 - Manufacturing of hydrochloric acid from salt and sulfuric acid



The purified hydrogen chloride is absorbed in absorption towers lined internally with material resistant to attack by concentrated hydrochloric acid.

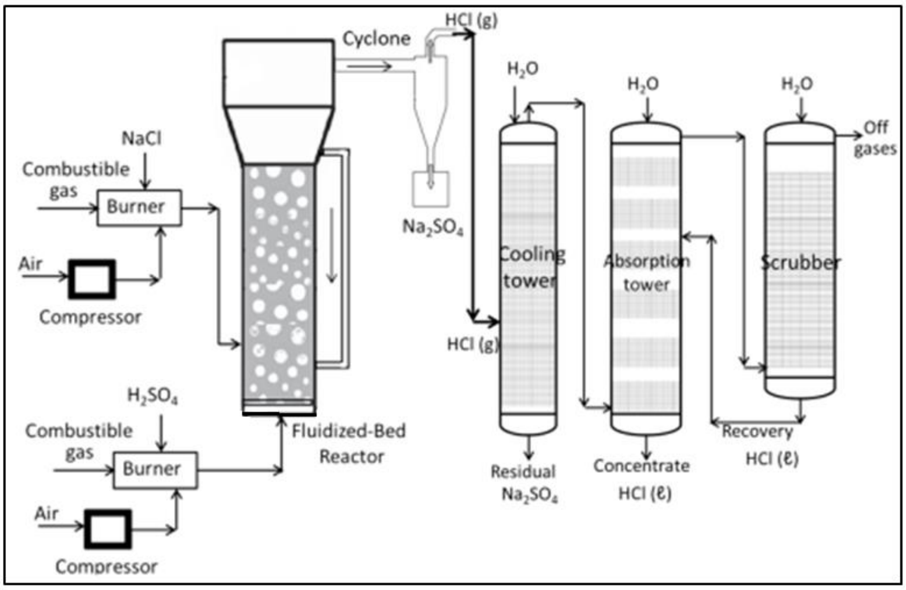
Salt-Acid Process with Fluidized Bed

In order to improve the performance of the process, acid salt is proposed to inject sulfuric acid vapor into a fluidized bed reactor with sodium chloride injection in the range of 500ºC, according to the following reactions:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$$

Figure 4 shows the fluidized bed reactor where hydrogen chloride and sodium sulfate formation occur. The cyclone separates the hydrogen chloride from gaseous hydrogen and sends it to the absorption towers for the formation of hydrochloric acid, while the sodium sulfate is recovered in solid form.

Figure 4 - Salt-Acid Process for hydrochloric acid with Fluidized-bed reactor



PROCESS FOR THE PRODUCTION OF POTASSIUM SULPHATE FROM POTASSIUM CHLORIDE AND SULPHURIC ACID

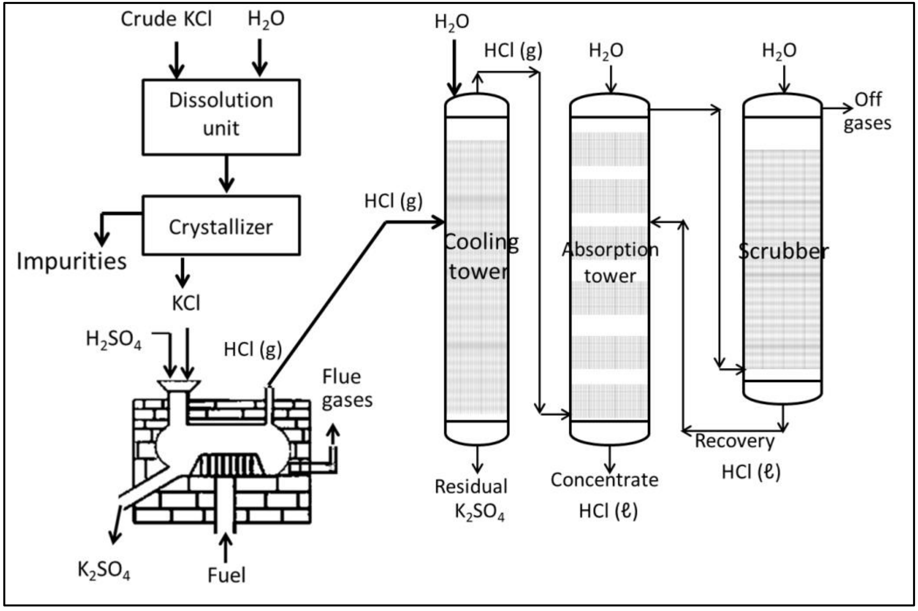
This process prioritizes the production of potassium sulfate as a fertilizer and hydrochloric acid as a byproduct. First, the crude potassium chloride is dissolved in water to remove the solid impurities and then directed to the crystallizer to remove the soluble impurities. Immediately afterwards, purified potassium chloride and sulfuric acid are injected into the Mannheim-type furnace in the temperature range between 300-400°C. Figure 5 shows the production process based on the following reactions [14, 15]:

Exothermic reaction: $KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$

$$\text{Endothermic reaction: } KCl + KHSO_4 \rightarrow K_2SO_4 + HCl$$

Or potassium sulfate is removed in solid form and hydrogen chloride flows into the Cooling Towers and absorption for the production of hydrochloric acid.

Figure 5 - Schematic diagram of potassium sulfate and hydrochloric acid



Potassium mineral deposits healthy sedimentary rocks, formed by the evaporation of saline water and found in various parts of the world. Generally, they are in the form of silvita (KCl), silvinita ($KCl.NaCl$) e carnalita ($KCl.MgCl_2.6H_2O$) [16, 17]. The main contaminants in the form of cations and anions present in these ores are: Ca^{2+}, Mg^{2+}, Fe^{2+}, SO_4^{2-}, Br^-, SiO_3^{2-}. and chloride ions can react with sulfuric acid and form $CaSO_4$, $MgSO_4$, $FeSO_4$, contaminating the sodium sulfate formed.

The reaction between KBr and H_2SO_4 can generate HBr (g) that flows along with HCl (g) and contaminates hydrochloric acid, depending on the reaction:

$$2\ KBr + H_2SO_4 \rightarrow K_2SO_4 + 2\ HBr$$

SYNTHETIC PROCESS FOR THE PRODUCTION OF HYDROCHLORIC ACID

This process developed in the 1940s has the great advantage of being extremely pure, since it comes from the direct burning of chlorine and hydrogen molecules from the electrolytic production of sodium chloride, in obtaining sodium hydroxide. Its technology was only possible from the development of materials resistant to high temperatures and the oxidizing conditions of this burning.

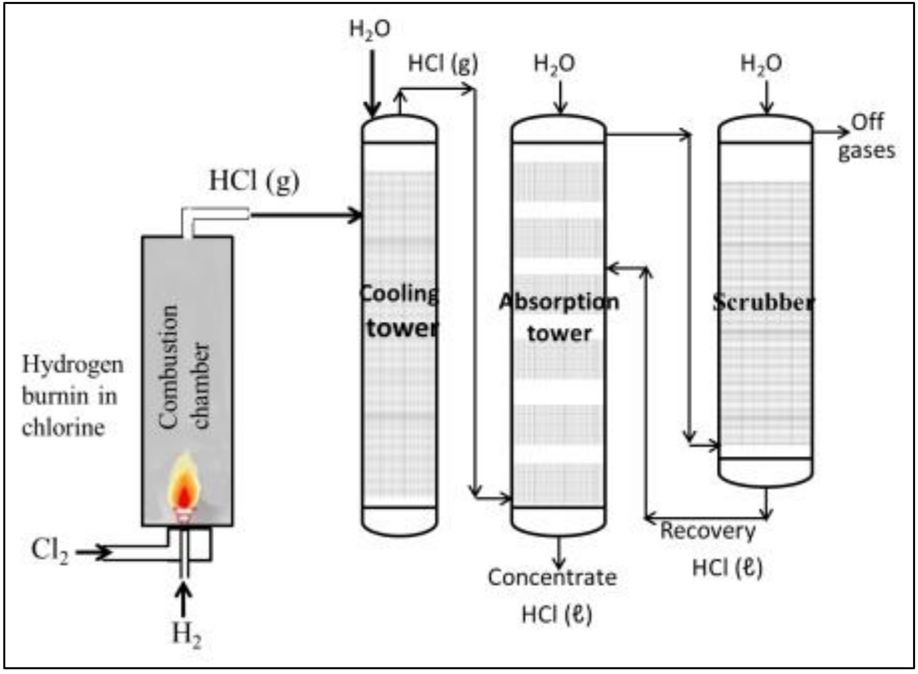
The reaction takes place in a vertical combustion chamber, with a structural carbon, lined with silica refractory bricks and provided with a continuous cold water cooling system [15, 18-20].

Generally, these combustion chambers have the shape of a cone trunk and a cap at the top, made of asbestos so that in the event of an explosion, this cap can break without compromising the structure of the reactor. The size of the chamber is dimensioned so that there is a complete reaction between the chlorine and hydrogen molecules as shown in the flowchart below in Figure 6.

To ensure a complete reaction with chlorine, an excess of 10% hydrogen is required. The reaction occurs at a temperature of 2,400°C with a greenish flame, and is represented by the following reaction:

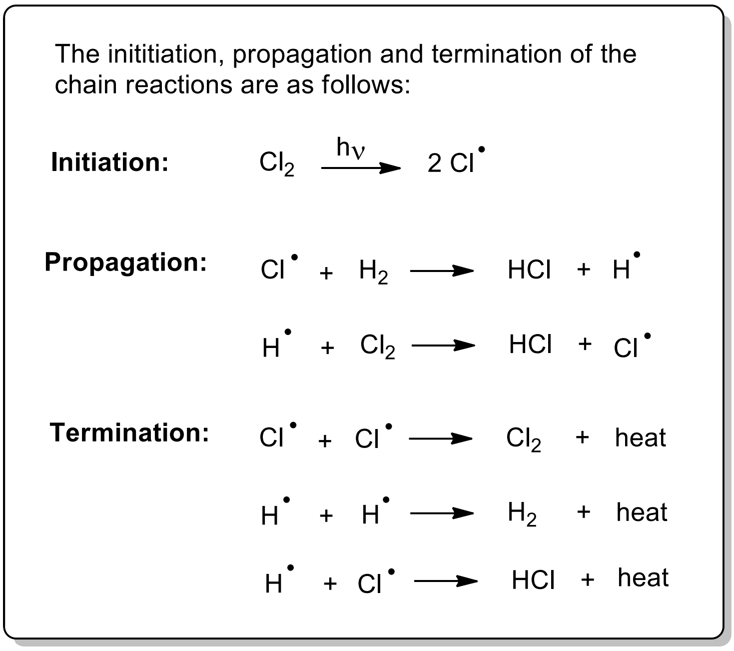
$$H_2 + Cl_2 \rightarrow 2\ HCl \quad (\Delta H = -\ 44.2\ kcal)$$

Figure 6 - Manufacturing of hydrochloric acid from hydrogen and chlorine combustion



The reaction is exothermic and propagates in the gas phase by alternating the following intermediate reactions, including the initiation, propagation and termination of chain reactions, as shown in Figure 7.

Figure 7 - HCl formation reactions at high temperature



The inititiation, propagation and termination of the chain reactions are as follows:

Initiation: $Cl_2 \xrightarrow{h\nu} 2\,Cl^{\bullet}$

Propagation: $Cl^{\bullet} + H_2 \longrightarrow HCl + H^{\bullet}$

$H^{\bullet} + Cl_2 \longrightarrow HCl + Cl^{\bullet}$

Termination: $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2 + \text{heat}$

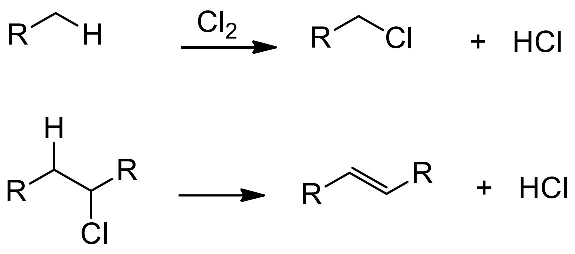
$H^{\bullet} + H^{\bullet} \longrightarrow H_2 + \text{heat}$

$H^{\bullet} + Cl^{\bullet} \longrightarrow HCl + \text{heat}$

Considering that the chlorine and hydrogen from the electrolytic cells are extremely pure, this production is characterized by obtaining a high purity hydrochloric acid. However, if H_2 and Cl_2 come from other processes, it is possible to contaminate the acid.

RECOVERY OF HYDROCHLORIC ACID FROM CHLORINATION OF ORGANIC COMPOUNDS

Since the 1960s, there has been an increasing use of hydrochloric acid from the chlorination of organic molecules or the decomposition of organochlorines, as shown in the following reactions:



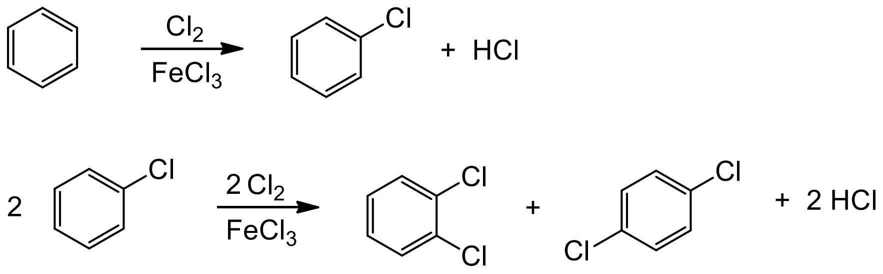
Mercado Libre Internacional offers hydrochloric acid for sale without identifying the origin of the process, and consequently does not report the presence of organochlorines. In order to evaluate the main contaminants in hydrochloric acid, some processes for obtaining organochlorine products and the recovery of hydrochloric acid are presented below.

Recovery of hydrochloric acid from monochlorobenzene and dichlorobenzene

The production of chlorobenzenes peaked in 1969, but its production has been falling precipitously due to its replacement by more environmentally friendly Chemicals. However, in the international scenario, such molecules have been used as additives, chemical intermediates in rubber, paints, anilines, insecticides, dyes, etc. [21].

The process of obtaining monochlorobenzene and dichlorobenzene consists of the reaction of chlorine with benzene in the presence of a ferric chloride catalyst ($FeCl_3$). Chlorine is bubbled at a temperature ranging from 40 to 60°C, so that the yield of monochlorobenzene synthesis varies between 60 and 75%, while that of dichlorobenzene is between 10 and 20%.

The reactions involved in this process are:



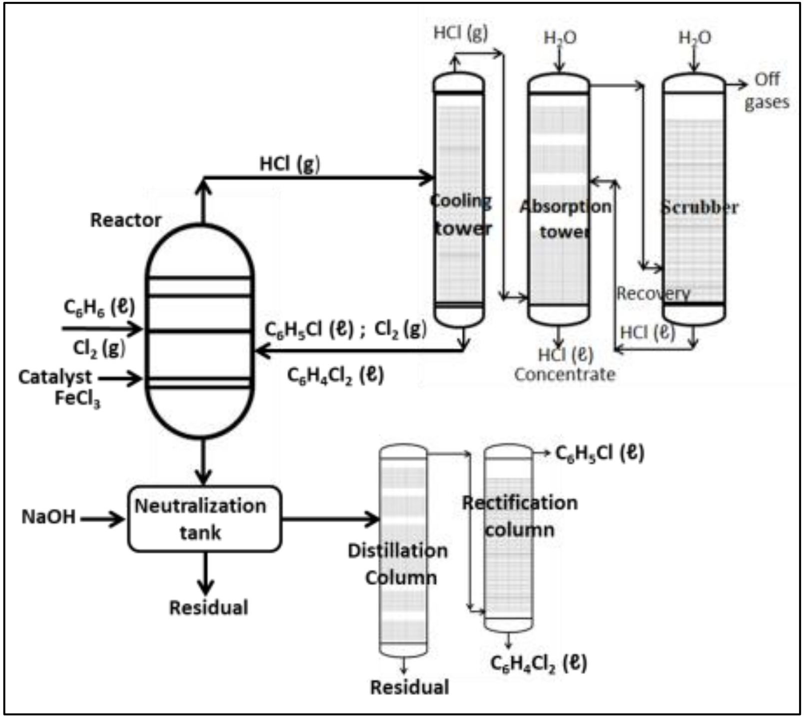
The simplified flowchart presented in Figure 8 shows that after the organochlorines are formed in the reactor, the hydrogen chloride passes through a condenser to retain the organochlorines, benzene, and chlorine to return to the chlorinator. Hydrogen chloride is absorbed in the absorption tower with water to form hydrochloric acid. The organochlorine products from the chlorinator pass through a neutralization tank to neutralize the traces of HCl and Cl_2, and then the organochlorines go to a distillation and rectification column to separate the monochlorobenzene from the dichlorobenzene.

The neutralization reactions that occur in the neutralization tank are:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$Cl_2 + 2\,NaOH \rightarrow NaClO + NaCl + H_2O$$

Figure 8 - Simplified flowchart of obtaining hydrochloric acid from benzene chlorination



As shown in the diagram shown in Figure 8, depending on the operating conditions or *by-pass*, the following contaminations are possible: C_6H_5Cl, $C_6H_4Cl_2$, Cl_2 and C_6H_6

Recovery of hydrochloric acid from the production of benzyl chloride

This product is used as a chemical intermediate in the manufacture of pharmaceuticals, especially in the synthesis of phenobarbital, benzedrine, etc. It is also used to obtain plasticizers for paints and the like [15, 22].

The process consists of the direct reaction of chlorine with toluene in a reactor with no light, as shown in the reaction and flowchart in Figure 9:

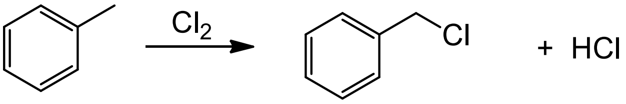
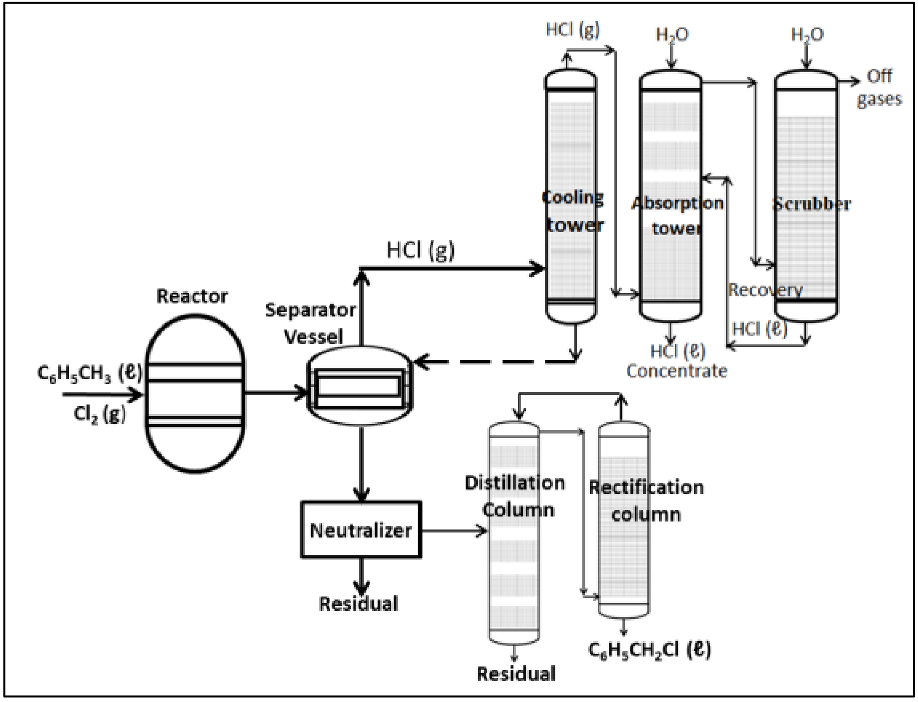


Figure 9 - Simplified flowchart of obtaining hydrochloric acid from toluene chlorination



The mixture consisting of benzyl chloride and hydrogen chloride, which comes out of the chlorination reactor, passes through a separator vessel where the hydrogen chloride gas stream is separated from the liquid phase consisting of benzyl chloride. Hydrogen chloride is absorbed into water, forming a hydrochloric acid solution.

Based on the production process, it is possible that the hydrochloric acid obtained in the absorption tower may be contaminated mainly with chlorine and toluene due to the recycle operation.

Recovery of hydrochloric acid from the process of obtaining carbon tetrachloride from organochlorine residues

Carbon tetrachloride (CCl_4) is used as a chemical intermediate in the rubber industry and as solvents in the chemical and pharmaceutical industries. However, its use has been questioned due to environmental contamination because it is considered as a volatile organic compound (VOC) [15, 22-24].

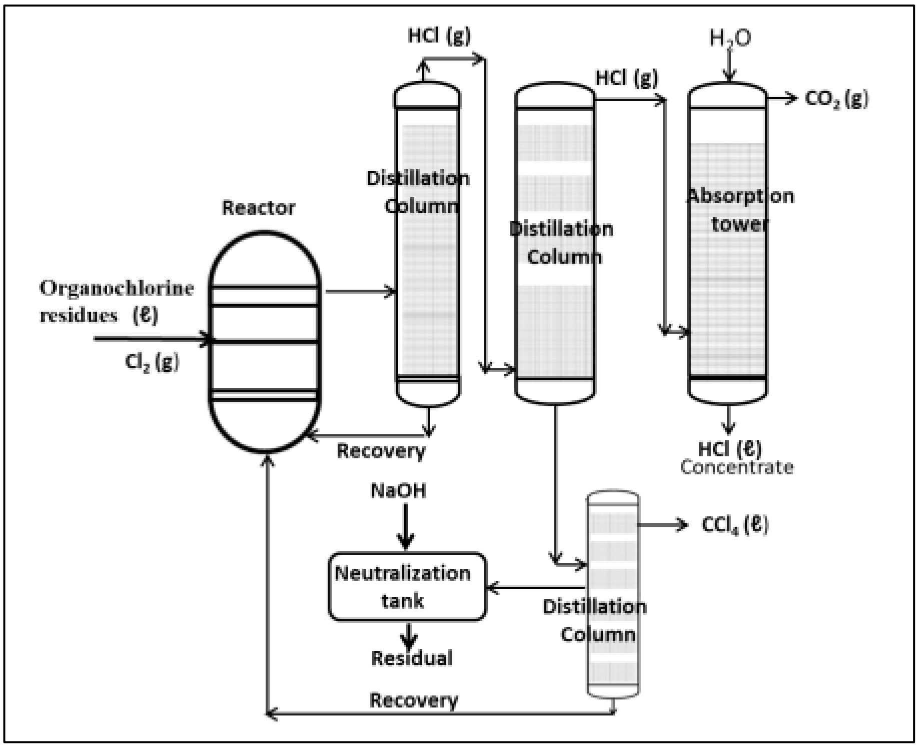
From the point of view of hydrochloric acid contamination, this is an interesting process, as it aims to transform various hydrocarbons and organochlorines into carbon tetrachloride.

The process consists of a direct reaction of mixing organochlorines with chlorine at a temperature of 600°C in a chlorination reactor, aiming at the production of carbon tetrachloride and hydrochloric acid, as shown in the reactions and the flowchart shown in Figure 10.

$$3\ Cl_2 + CH_3\text{-}Cl \rightarrow CCl_4 + 3\ HCl$$

$$2\ COCl_2 \rightarrow CCl_4 + CO_2$$

Figure 10 - Simplified flowchart of hydrochloric acid recovery from obtaining carbon tetrachloride from organochlorine residues



Considering the origin of this raw material (organochlorine compounds) it is possible to visualize organochlorines and chlorine as possible contaminants of hydrochloric acid obtained in the absorption tower.

Recovery of hydrochloric acid from the process of obtaining dichlorodifluoromethane (Freon-12)

Currently, the industrial production of some organochlorofluorinated products has been discontinued due to environmental problems. However, some international units still exist, considering the demand for the product without the environmental concern, typical of international free markets.

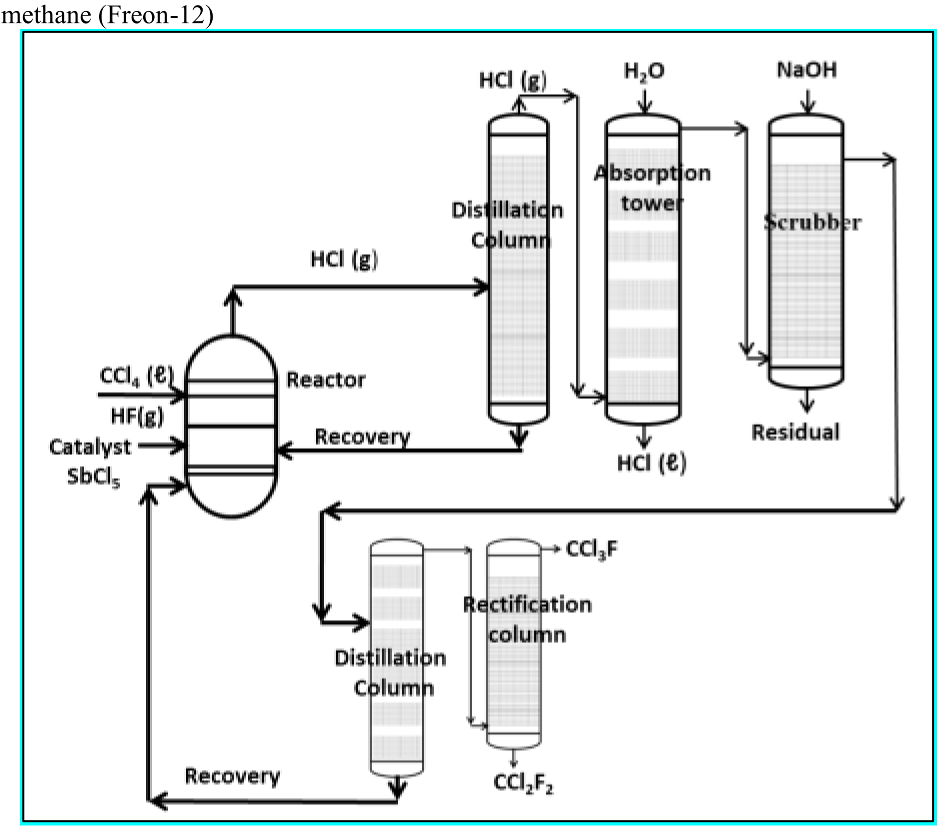
The industrial production process consists essentially of the bubbling of hydrogen fluoride (HF), anhydrous, and carbon tetrachloride in used antimonic pentachloride ($SbCl_5$), which acts as a catalyst for the reaction. Depending on the molar relationship, dichlorodifluoromethane and trichloromonofluoromethane may be formed. The reactions are endothermic and occur in the temperature range of 65 to 100°C and in the presence of the catalyst [25].

$$CCl_4 + HF \rightarrow CCl_3F + HCl$$

$$CCl_4 + 2\,HF \rightarrow CCl_2F_2 + 2\,HCl$$

The hydrogen chloride produced in the reaction is removed through an absorption tower with water and the possibility of contamination with hydrogen fluoride with hydrofluoric acid formation. HF levels can vary between 100 and 1,000 ppm.

Figure 11 - Simplified flowchart of the recovery of hydrochloric acid from the process of obtaining dichlorodifluoromethane (Freon-12)



ANALYSIS OF CONTAMINANTS FROM HYDROCHLORIC ACID PRODUCTION PROCESSES

As previously mentioned, hydrochloric acid is a basic input used in the various industrial segments. It is offered in the international free market as concentrated solutions at 37 wt.% (by mass), of high purity for analytical, pharmaceutical and food industry purposes; as well as in commercial concentrations ranging from 10 to 30% wt.%.

The Material Safety Data Sheet (MSDS) [26] shall accompany the sale of hydrochloric acid for various purposes and shall have 16 sections identified as: (a) Identification of Chemicals and Companies; (b) Composition and information on ingredients; (c) identification of hazards; (d) first aid measures; (e) data on fires and explosions; (f) Accident clearance measures; g) Handling and storage; h) Exposure/personal protection controls; (i) physical and chemical properties; (j) stability and reactivity data; (k) toxicological information; (l) ecological information; (m) disposal considerations; (n)transport information; (o) other regulatory information; (p)other information.

Data sheets do not always report the contaminants, the production process, and the raw material used. Therefore, the objective of this study is to identify and quantify the main industrial processes, the possible contaminants that may be present in hydrochloric acid solutions. Thus, criteria are proposed in which the possibilities of occurrence of contaminants with their levels are established, aiming at their use in various industrial segments (Table 1).

The possibility of contaminants existing in the processes of obtaining hydrochloric acid will depend on several direct or indirect factors, although the raw material is the most important, as it can aggregate the contaminants and pass them on to the acid.

Table 1 - Possibility of contaminants and hydrochloric acid

Possibility of contaminants	***Legend***
Very likely	VL
Possible	PO
Very unlikely	VU
Unlikely	UN

Table 2 shows the probable levels of contaminants that may be added to the hydrochloric acid solution.

Table 2 - Level of probable contaminants in hydrochloric acid solution

Level of contaminant (ppm)	***Legend***
0 – 1	A
1 – 10	B
10 - 100	C
100 - 1000	D
> 1000	F

The main contaminants that may be present in hydrochloric acid will be analyzed, below:

TOTAL IRON

Generally, the total iron found in chemical analyses of hydrochloric acid is referred to as total iron, considering it in the form of Fe^{2+} (ferrous) and Fe^{3+} (ferric). The Fe^{2+} ion may come from the contamination of sodium chloride obtained from solar evaporation from seawater or from the mining of rock salt [10-13]. Another possibility is the acid attack on carbon steel pipes, generating ferrous chloride according to the reaction:

$$Fe + 2\,HCl \rightarrow FeCl_2 + H_2$$

The occurrence of the ferric ion can be explained by the oxidation of the Fe^{2+} ion, by means of oxygen solubilized in hydrochloric acid. The high concentration of H^+ ions does not favor the oxidation of Fe^{2+} to Fe^{3+}, but as the concentration of H^+ ions decreases, there is a tendency for hydrolysis of ferric ions and, consequently, an increase in the oxidation rate. The transformation of ferrous chloride to ferric chloride can be evidenced by the reaction:

$$4\ FeCl_2 + 4\ HCl + O_2 \rightarrow 4\ FeCl_3 + 2\ H_2O$$

If chlorine (Cl_2) is present in the acidic solution, ferrous chloride can be oxidized to ferric chloride based on the reaction:

$$2\ FeCl_2 + Cl_2 \rightarrow 2\ FeCl_3$$

The total iron contents vary from 0.2 to 10 ppm, however, in some commercial hydrochloric acids offered in the International Free Market these values can be higher than 100 ppm.

CHLORINE AND ORGANOCHLORIDE

Free chlorine (Cl_2), present in hydrochloric acid solutions, can come from a synthetic process or from hydrochloric acid recovery processes from the chlorination of organic substances. However, it is impossible for chlorine to come from processes that have sodium chloride or potassium chloride as raw material.

In the synthetic process, the occurrence of chlorine is due to the incomplete reaction of hydrogen with chlorine, in such a way that there is an excess of chlorine that is solubilized in the acid solution, while the hydrogen, due to its low solubility, is given off, and thus does not solubilize in the acid solution.

In the hydrochloric acid recovery process, the presence of free chlorine in the acid solution is due to the deficiencies that occurred during the separation and purification process, that is, it depends on the efficiency of the gas separation processes.

The chlorine content, present in commercial acids, is in the range of 2 to 10 ppm, although values of up to 50 ppm have been observed, mainly in commercial hydrochloric acid recovered from chlorination processes.

The presence of organochlorines in hydrochloric acid recovered from chlorination processes of organic substances is usually due to operational deficiencies in the extraction and purification system of the recovered acid. The contaminant content is a function of the reactions involved and the solubility of these chlorinated compounds in the hydrochloric acid produced. Organochlorine concentrations can range from 5 to 1,000 ppm.

BROMINE AND HYDROBROMIC ACID

The occurrence of bromine (Br_2) and hydrobromic acid (HBr) in hydrochloric acid solution can be explained by supposing that this acid comes from the salt-acid process. The sodium chloride used as a raw material can be extracted from rock salt mining, which depending on the rock formation may contain sodium bromide (NaBr).

Sodium bromide, when reacting with H_2SO_4 at high temperatures, can generate Br_2 and HBr, as shown by the following reactions:

$$2\ NaBr + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HBr$$

$$2\ HBr + H_2SO_4 \rightarrow SO_2 + Br_2 + 2\ H_2O$$

Br_2 and HBr can be entrained into the hydrochloric acid absorption tower and absorbed as a contaminant in this acid. The concentration of bromide (HBr) can be in the range of 0.01 to 10 ppm.

FLUORIDE AND ORGANOFLUORINES

The occurrence of fluoride (F^-) or in the form of hydrofluoric acid (HF) occurs in salt-acid processes, in the recovery of hydrochloric acid from the fluoridation of organic compounds (Figure 11). The occurrence of HF only does not occur in the synthetic process.

Considering that the saline raw material may contain sodium fluoride (NaF) and/or calcium fluoride (CaF_2) and the reactions that occur with H_2SO_4 in the salt-acid process are as presented, as follows:

$$2\ NaF + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HF$$

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF$$

Hydrogen fluoride (HF) gas can escape from the furnace and be drawn into the hydrochloric acid absorption tower, being absorbed and incorporated as a contaminant into this acid. In the organofluorines production process, HF (g) can be entrained into the hydrochloric acid absorption tower and be incorporated as a contaminant.

Chemical analyses carried out on commercial acids offered in the International Free Market have shown values even higher than 1,000 ppm in HF.

SULPHATE

Generally, the occurrence of sulfate in hydrochloric acid solutions is due to the absence of H_2SO_4 droplets and solid Na_2SO_4 particles that accompany the detachment of hydrogen chloride in salt-acid processes. Chemical analyses reveal values from 10 to 1,000 ppm that depend on the operating conditions of the process.

PHOSPHATE

The occurrence of phosphate (PO_4^{3-}) or phosphoric acid (H_3PO_4) in hydrochloric acid solutions is unlikely. However, contaminations can be admitted if the H_2SO_4 used in the salt-acid process is contaminated by phosphoric acid. Such a possibility could occur in the recovery of sulfuric acid from the fertilizer industry, where the reaction would occur:

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \rightarrow 3\ CaSO_4 + 2\ H_3PO_4$$

LEAD

The occurrence of Pb^{2+} ions in hydrochloric acid solutions is practically unlikely, as such contaminant is not related to industrial manufacturing routes. In the case of salt-acid processes that use sulfuric acid, the only possibility would be the use of a sulfuric acid contaminated with this ion. For example, the recovery of lead batteries and the H_2SO_4 associated with the process could result in probable contamination.

Another possibility of finding Pb^{2+} ions would be the attack on the lead gaskets used in bombs by hydrochloric acid, resulting in lead chloride, as shown in the reaction:

$$Pb + 2\ HCl \rightarrow PbCl_2 + H_2.$$

SODIUM

Na^+ ions are not usually present in hydrochloric acid solutions, however, it has been observed in commercial hydrochloric acid offered in the International Free Market. This is due to fraudulent additions of sodium chloride in order to increase the density of the acid and in a way to evade the increase in acid concentration. Some samples analyzed showed sodium values higher than 1,000 ppm.

ORGANIC COMPOUNDS

In recycle operations, during the recovery of hydrochloric acid from chlorination and/or fluorination of organic compounds, it is possible that these molecules detach and are incorporated into the acid stream at the hydrochloric acid absorption tower. Some organic compounds can also solubilize in small amounts in acidic solutions, such as: benzene, toluene, methyl alcohol and etc.

The levels of hydrocarbons present in hydrochloric acid solutions can vary from 1 to 100 ppm, which will depend on the efficiency of the removal process as shown in Figures 9 to 11.

Based on Tables 1 and 2, which present the possibility of contamination and contamination levels, Table 3 was constructed, interrelating these indices with the main hydrochloric acid production processes.

Table 3 - Matrix of the possibility and levels of contaminants with the main hydrochloric acid production processes

Contaminants	***Possibility and level of contaminants***			
	Salt-Acid Process	Synthetic process	Recovery of HCl from chlorination of organic compounds	Recovery of HCl from fluorination of organic compounds
Fe^{2+} (ferrous)	VL,C	PO,B	PO,B	PO,B
Fe^{3+} (ferric)	VL,C	PO,B	PO,B	PO,B
Chlorine (Cl_2)	UN	PO,B	PO,C	PO,B
Organochlorine	UN	UN	PO,D	PO,B
Bromine (Br_2)	VU,A	UN	VU,A	VU,A
Hydrobromic acid (HBr)	VU,A	UN	VU,A	VU,A
Hydrofluoric acid (HF)	VL,E	UN	VU,A	VL,C
Organofluorines	UN	UN	VU,A	VL,C
Sulfate (SO_4^{2-})	VL,E	UN	VU,A	VU,A
Phosphate (PO_4^{3-})	PO,A	UN	UN	UN
Lead (Pb^{2+})	VU,A	UN	UN	UN
Sodium (Na^{+})	UN	UN	UN	UN
Organic Compounds	UN	UN	PO,C	PO,C

LEGEND 1: (VL) Very likely ; (PO) Possible; (VU) Very unlikely; (UN)Unlikely.
LEGEND 2: A (0–1 ppm); B (1–10 ppm); C (10-100 ppm); D (100-1.000 ppm);
B (> 1.000ppm)

USE AND INFLUENCE OF HYDROCHLORIC ACID IN INDUSTRIAL PROCESSES

As shown in Figure 2, hydrochloric acid is used in various industrial segments including the manufacture of food, pharmaceuticals, dyes, metal chlorides, pickling of metal products, among others, and is also injected into oil wells to remove calcareous scale in order to increase their oil and natural gas.

Table 4 shows the results of hydrochloric acid analysis in four samples used as examples for industrial purposes offered in the International Free Market and called: Food Grade, Commercial 01, Commercial 02 and Commercial 03.

Table 4 - Hydrochloric acid analysis of samples offered on the International Free Market

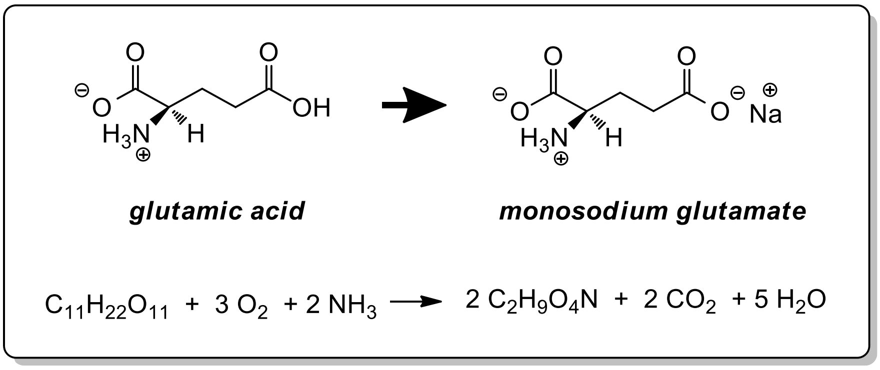
Contaminants	***Food Grade***	***Commercial 01***	***Commercial 02***	***Commercial 03***
Assay, wt.%	37.0	32.4	27.4	15.2
Density, 20°C, g/cm^3	1.19	1.16	1.14	1.11
Iron as Total Fe, ppm	0.1	0.1	25	35
Chlorine (Cl_2), ppm	0	13.1	10.3	15.2
Organochlorine	0	13.1	10.3	15.2
Bromine (Br_2)	0	0	2.0	1.5
Hydrobromic acid (HBr)	0	0	0	0
Hydrofluoric acid (HF)	0	0	25	23
Organofluorines	0.1	10	50	34
Sulfate (SO_4^{2-})	0	< 1.0	< 2.0	< 2.0
Phosphate (PO_4^{3-})	0	0	0	0

To evaluate the use of hydrochloric acid as a function of possible contamination, the industrial production of the food additive (monosodium glutamate) and acid injection in oil wells were chosen. The use of contaminated acids in the process can result in final products with contamination, which in most cases, are not listed in the technical specifications and that can cause problems to public health, the environment or the process itself with great losses.

INDUSTRIAL ASSESSMENT OF MONOSODIUM PRODUCTION

Monosodium glutamate (Figure 12) is a sodium carboxylate, i.e., an organic salt derived from glutamic acid, obtained by fermentation of carbohydrates. It is an important condiment used in food. Although it does not have a taste of its own, it has the function of accentuating the flavors of food by enhancing sensory perception, particularly the aromas of meat and derivatives in canned goods, ready-to-eat soups, sausages, etc. [27-31].

Figure 12 - Schematic structure of glutamic acid and monosodium glutamate



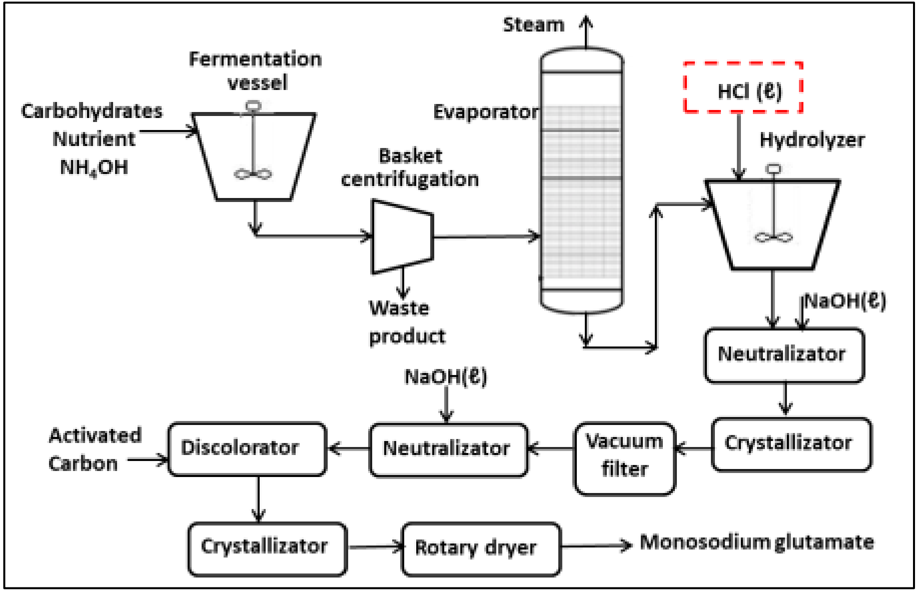
The fermentation process for the production of monosodium glutamate is represented by the simplified flowchart in Figure 13, consisting of the following steps:

a) Concentration and preparation of fermentative matter.
b) Hydrolysis with the addition of sodium hydroxide.
c) Acidification with hydrochloric acid.

d) Removal of inorganic acids formed by the action of hydroxide with acid.
e) Crystallization, separation and purification of the formed glutamic acid.
f) Neutralization with sodium hydroxide.
g) Deodorization.
h) Crystallization, centrifugation, and drying of the final product (27, 28).

In the process of obtaining monosodium glutamate (Figure 13), it is verified that hydrochloric acid is added to the hydrolyzer in order to form glutamic acid. This means the need to use hydrochloric acid with high purity. If an acid with impurities is used, it is clear that the monosodium glutamate will incorporate these contaminants into the final product. As a result, the final product will become a public health problem.

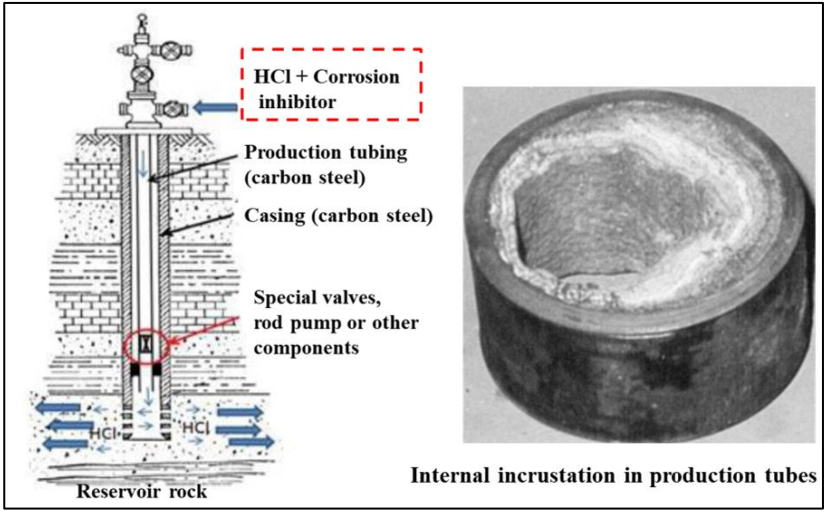
Figure 13 - Simplified flowchart of monosodium glutamate production



ASSESSMENT OF ACIDIFICATION OF OIL WELLS

The acidification of oil wells, also called acid stimulation, comprises the injection of hydrochloric acid (10 to 28%) into the reservoir rock, aiming to increase the productivity of the well. In addition, this injection also dissolves the internal fouling in the oil and natural gas production pipes. The injection of the acid into the well and the internal fouling in the tubes are shown in Figure 14.

Figure 14 - Acid injection in oil wells



The main determination of this process is to remove wellbore formation damage, promoting the dissolution the reservoir rock and consequently increasing the permeability of rock to the passage of oil & natural gas. [32, 33]. HCl is the most widely used in acidifications due to its ease of dissolving carbonate rocks, such as limestone ($CaCO_3$) and dolomite ($CaCO_3$. $MgCO_3$). The formation of soluble salts ($CaCl_2$ and $MgCl_2$) occurs when HCl penetrates the reservoir rock, as shown by the following reactions:

$$2\,HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$$

$$4\,HCl + CaCO_3.MgCO_3 \rightarrow CaCl_2 + MgCl_2 + 2\,CO_2 + 2\,H_2O$$

The injection of hydrochloric acid is done by the production pipe and fittings which are made of carbon steel (Figure 14), while other equipment involved in the operation (valves, rings, special pump, etc.), are usually stainless steel. To prevent the corrosion of these materials, it is essential to add a corrosion inhibitor, whose function is to avoid or minimize the accentuated attack of hydrochloric acid on metallic materials.

An oil well is worth thousands of dollars and damage to the permeability of the reservoir rock can mean the total loss of the well, i.e. the loss of production. On the other hand, if there is corrosion of the pipes and equipment involved, the cost is also very high. The equipment can be exchanged or recovered, but in most cases, the damage to the reservoir rock, the recovery of the well is irrecoverable.

In view of this catastrophic scenario, it is essential to use a hydrochloric acid that meets a specification and that does not cause damage to oil production or equipment corrosion. Thus, it is essential that the maximum levels of iron, sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), chlorine (Cl_2) and organochlorines do not exceed the values presented in Table 5.

The SO_4^{2-} and PO_4^{3-} ions present in hydrochloric acid can react with the Ca^{2+}, Sr^{2+} and Ba^{2+} ions in oil production waters and precipitate the respective sulfates ($CaSO_4$, $SrSO_4$, $BaSO_4$) and phosphates [$Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ba_3(PO_4)_2$], as they are insoluble and can occlude and buffer the flow of fluids.

According to the literature, laboratory tests performed with carbon steel specimens and with additions of ferric ions (Fe^{3+}) and free chlorine (Cl_2) in high purity hydrochloric acid, conclude that such substances can affect the performance of the protection exerted by corrosion inhibitors [34-36].

Table 5 - Maximum concentrations of contaminants that may be present in hydrochloric acid solution for acidification operations in oil wells

Maximum concentrations of contaminants (%)	***Value***
Iron as Total Fe	0.002
Chlorine (Cl_2)	0.0005
Organochlorine	0.0005
Sulfate (SO_4^{2-})	0.005
Phosphate (PO_4^{3-})	0.002

EXAMPLES OF EXPERIMENTS SHOWING THE INFLUENCE OF THE EXISTING CONTAMINANT ON HYDROCHLORIC ACID

In order to demonstrate that some contaminations present in hydrochloric acid can, directly or indirectly, contaminate the process or the final product, laboratory experiments were developed for this purpose.

PRECIPITATION OF BARIUM SULPHATE AND STRONTIUM SULPHATE IN PETROLEUM PRODUCED WATER CONTAINING BA^{2+} AND SR^{2+} IONS

This simple experiment seeks to demonstrate that the acidification of an oil well with hydrochloric acid can become a problem related to scale or insoluble deposition when hydrochloric acid contaminated with sulfate encounters a oilfield produced water containing Ba^{2+} and Sr^{2+} ions.

The simulated oilfield produced water for laboratory tests is considered as a saline solution containing 20 wt.% of NaCl, 200 mg/L of $SrCl_2$ and 100 mg/L of $BaCl_2$ representing respectively, 110 mg/L of Sr^{2+} and 66 mg/L of Ba^{2+} .

Three 15 wt.% solutions of high-purity hydrochloric acid were prepared. The first is sulfate-free, the second is 400 mg/L of Na_2SO_4 is added, and the third is 800 mg/L of Na_2SO_4. Then, 10 mL of each acid solution were poured into three test tubes containing 10 mL of produced oilfield produced water containing Ba^{2+} and Sr^{2+} ions. It was found that in the first tube there was no precipitate formation, while in the other two there was an intense white precipitation, due to the formation of strontium sulfate and barium sulfate, represented by the reactions:

$$SrCl_2 + Na_2SO_4 \rightarrow SrSO_4 + 2\ NaCl$$

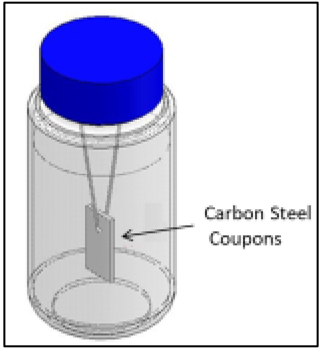
$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2\ NaCl$$

It is concluded that the formation of insoluble sulfates can compromise the acidification operation.

EVALUATION OF THE ACTION OF FERRIC IONS PRESENT IN HYDROCHLORIC ACID USED IN THE ACIDIFICATION OF AN OIL WELL OR IN THE PICKLING OF CARBON STEEL

The test consists of the total immersion of carbon steel coupons (dimensions: 45 x 15 x 1.2mm) in a glass container (Figure 15), at a temperature of 65°C, for 1 h in 15% wt.% of hydrochloric acid containing 100, 500, 1,000 and 5,000 mg/L of Fe^{3+} and additions of 300, 500 and 1,000 mg/L of corrosion inhibitor. The corrosion inhibitor used in these tests is a mixture of 70 wt.% of propargyl alcohol, 20% wt.% of high molecular and 10% wt.% of solvent. The corrosion rate is calculated by the mass loss of the coupons before and after the test.

Figure 15 - Immersion mass loss test of carbon steel specimens in 15 wt.% hydrochloric acid solution



Three coupons were used to verify the reproducibility of the results. The corrosion rate (CR) was defined by the following expressions:

$$\text{Corrosion rate} = CR = (Wo - Wi)/S.\ h\ (mg/cm^2.h).$$

Where: Wo and Wi are the mass losses in the absence and presence of the corrosion inhibitor.

The laboratory results shown in Table 6 demonstrate that the ferric ion interferes with the protective action exerted by the mixture of corrosion inhibitors, increasing the mass loss of carbon steel, i.e., decreasing the efficiency of the inhibitor. The corrosion inhibitor reduces acid attack, but does not prevent the attack of oxidizing agents such as ferric ions present in the acid solution. The experiment also demonstrates that the presence of ferric ions in hydrochloric acid can act as an oxidant, reducing the efficiency of the corrosion inhibitor and can, in theory, compromise the acidification of the oil well.

Table 6 - Results of tests of weight loss of carbon steel coupons in 15 wt.% of HCl at 65 °C, with addition corrosion inhibitor (70 wt.% propargyl alcohol, 20 wt.% high molecular weight amines and 10 wt.% solvent)

Corrosion inhibitor concentration (mg/L)	***Mass loss, mg/cm^2.h***				
	Concentration of ferric ions, Fe^{3+}, mg/L				
	0	100	500	1000	5000
300	0.50	0.55	0.80	3.10	7.50
500	0.30	0.40	0.70	2.55	6.85
1000	0.25	0.35	0.55	1.50	5.45

EVALUATION OF THE CHLORINE ACTION OF HYDROCHLORIC ACID USED IN THE ACIDIFICATION OF AN OIL WELL OR IN THE PICKLING OF CARBON STEEL

The test consists of total immersion of carbon steel coupons (dimensions: 45 x 15 x 1.2mm) in a glass container (Figure 15), at a temperature of 60°C, for 1 h in a solution at 10 to 15% wt.% of hydrochloric acid containing 100, 500, 1,000 and 1,500 mg/L of chlorine (Cl_2) and the addition of 1,000 mg/L of corrosion inhibitor. The corrosion inhibitor used in these tests is propargyl alcohol. Chlorine was added to hydrochloric acid in the form of calcium hypochlorite.

The corrosion rate was calculated by the mass loss of the coupons before and after the test.

The laboratory results presented in Table 7 attest that chlorine (Cl_2) interferes with the protective action exerted by the corrosion inhibitor, increasing the mass loss of carbon steel, i.e., decreasing the efficiency of the inhibitor. These facts are based on studies carried out by several researchers.

Table 7- Results of tests of weight loss of carbon steel coupons in 10 at 15 wt.% of HCl at 60 °C, with addition corrosion inhibitor (propargyl alcohol)

Chlorine (Cl2) concentration, mg/L	***Mass loss, mg/cm^2.h***	
	10 wt.% HCl	15 wt.% HCl
0	0.478	0.595
100	0.585	0.778
500	0.703	0.790
1000	0.748	1.033
1500	0.854	1.683

The referenced literature show that propargyl alcohol based corrosion inhibitors show excellent performance in protecting carbon steel in hydrochloric acid solutions at all concentration and temperature combinations [37 - 39].

The corrosion protection capacity is based on good adsorption capacity of propargyl alcohol molecules by carbon steel is linked to their π-electrons, which interact with metal surfaces and, consequently, form triple bonds, HC≡C-CH-OH [40]. It can be concluded that certain levels of chlorine in hydrochloric acid cause problems in the corrosion protection of equipment related to acidification operations in oil wells.

CONCLUSIONS

Based on the study, it is concluded that:

- It is necessary to develop a critical technical awareness that must be built in society, especially in the University, aiming at the understanding of industrial routes and the possible aggregations of contaminants during industrial processing.
- It is essential that the formation of critical technical awareness can determine, based on quality assurance, the correct use of hydrochloric acid solutions in the various industrial segments.
- It is important that general and specific quality criteria are set, culminating in a responsibility that unites the acid manufacturer, the intermediate product manufacturer and finally the end customer.
- Laboratory tests have shown that some contaminants present in hydrochloric acid used in acidification operations can cause fouling or corrosion problems, preventing or restricting the protective action exerted by corrosion inhibitors in acidic media.
- Finally, it is important to reinforce the use of hydrochloric acid from the synthetic process, i.e. of high purity, in the production of food and pharmaceutical products.

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