The teaching of chemical technologies associated with industrial contamination that impacts the environment

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ABSTRACT

This work aims to demonstrate the importance of knowledge for the formulation of clean technologies in the production of materials and chemical products, which do not go against the interests of society and are centered on environmental preservation. Most chemical processes were conceived at the beginning of the century or in the 1950s, where the principles of preservation of man, the environment and industrial safety were not fundamental requirements in the implementation of these large basic industries. The origin of the raw materials and the multiple industrial technologies adopted in the manufacture of various products and the recovery of industrial waste or other origins are fundamental factors that dictate the quality of the final product. Several industrial processes were presented where the level and type of contaminant is inseparably linked to its origins and the industrial processes imposed. In addition, it is concluded that it is important to develop a critical technical awareness in society, especially in the University, which aims to understand the manufacturing routes of the products and the contaminants generated and/or aggregated during industrial processing, especially in relation to the quality of the products and environmental preservation.

Keywords: Contamination, Chemical process, Environment, Industrial waste.

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INTRODUCTION

In current reflections, it is essential to delve into the near past and bring to the present important considerations that must be critically evaluated from the perspective of the problems that are linking and hindering the current paths of society.

There is no doubt that the socio-economic evolution of the global system, which partly involves agriculture, mineral exploration and oil & natural gas, industries (steel, metallurgical, oil refineries, petrochemicals, etc.), transportation and the disorderly occupation of large urban centers, has shown its influence on the environment, when taking into account the risks that each system faces. directly and/or directly, it may constitute.

In ancient civilizations, the Roman Empire and ancient Greece produced lead, copper, silver, and bronze (copper-tin alloy) through the primitive foundry or casting of their sulfide ores that released sulfur dioxide (SO_2) and carbon dioxide (CO_2) into the atmosphere.

The following are the reactions that occurred in the primitive foundry or casting of the order of 500 ºC where Galena Ore (PbS – lead sulfide) was oxidized and reduced to liquid lead:

$$PbS\ (s) + 3/2\ O_2\ (g) \rightarrow PbO\ (s) + SO_2\ (g)$$

$$PbO\ (s) + 2\ C\ (s) \rightarrow Pb\ (l) + CO_2\ (g)$$

In this Roman era, lead was the most popular metal and was widely used in everyday life. Many utensils such as glasses, jugs, and pans were made of lead alloys. These primitive foundry or casting were located in uninhabited areas and far from the city. However, the stench and aggressiveness of these toxic fumes spread throughout the region. In addition, the waste (slag) from these smelters was dumped on the outskirts of the city or into nearby rivers. There was no concern about lead contamination during early smelters, however, the Romans knew of the deaths that occurred in the lead mines [1,2].

Historical accounts also show that, along with the primitive foundry or casting, olive oil mills, slaughterhouses and tanneries were located far from the city to avoid the stench. However, with the growth of cities, such systems became closer and closer, aggressiveness and discomfort with bad smell returned to bother and worry; Then, the city governor ordered the transfer of the polluting segments farther away. As the city grew, the environmental problem continued. New displacements were ordered to more distant points, that is, the problem was not solved, but moved to the more distant surroundings.

In this way, it is evident that the degradation of the environment in all aspects did not arise suddenly, but accumulated throughout distant history. However, in the last seventy years, man has observed, participated or has been waiting for the development of industrial processes and energy generation, the creation or production, directly and/or indirectly, of a series of chemical products, materials and equipment used in daily life and in most industrial segments. In this way, chemical accidents, the production of inappropriate materials and chemical and biotechnological waste dumped into the environmental system have left marks of destruction in various parts of the planet.

From this point of view, it is not enough to monitor and report on the pollution problems that hang over cities. It is essential to have an active environmental policy and environmental management aimed at the preventive resolution of the environmental impacts generated, mainly, by chemical accidents that have occurred in industrial complexes and also by spills, leaks and contamination caused by oil pipelines and road, rail and maritime transport of flammable, toxic or explosive products. However, micro and small contaminations go unnoticed by industrial control systems and are not questioned by the knowledge that should be the basis of the fundamental premises of a project and consequently of an industrial process.

It is worth highlighting in this article the railway leaks of sulfuric acid to the environment that occurred in various parts of the world, as shown in the photo panel presented in Figure 1 [3-6]. Sulfuric acid, the object of these leaks, is the main agent in the production of phosphate fertilizers, sulfates and sulfonic derivatives.

According to Fortier [3], on September 23, 2021, in Attleboro, Massachusetts, USA, there was a leak of 5 thousand gallons (19 thousand liters) of sulfuric acid into the environment, a chemical product that was destined for a chemical industry in the region.

Ervin & Smith [4] report a derailment of about 40 cars on June 29, 2019, and a consequent leak of 13,700 gallons (52,000 liters) of sulfuric acid in an international train tunnel connecting the city of Sarnia, Ontario, Canada and the city of Port Huron, Michigan, USA.

The Guardian [5] describes a derailment that occurred on 29 December 2015 of a 26-car train carrying 600,000 litres of sulfuric acid, of which 30,000 litres leaked into the environment. On 17 February 2013, there was another derailment of 12 wagons in the Urals region (Russia) with sulfuric acid spreading over an area of 100 m^2 [6].

Due to the great development of chemical processes, the situation becomes progressively more serious, when considering the annual launch of more than 8,000 new formulations in the world market, including new detergents, disinfectants, pharmaceuticals, fragrances, personal care products, dietetic products, lubricants, paints, fertilizers, pesticides, among others. Such products exert strong pressure on the environment, in view of the risks inherent to their manufacturing processes, such as: effluents, leaks, recycling, toxic waste, etc.

Figure 1 - Examples of sulfuric acid rail leaks in various parts of the world

Source: A: Fortier [3]; B: Erwin & Smith [4]; C: The Guardian [5]; D: RT [5].

For example, according to Kalyabina *et al.* [7] Pesticides are formulated with a wide variety of chemicals, which are increasingly being used around the world. In this research, it is reported that the European Union, in 2021, considered 1378 active chemicals, of which 466 were approved and 858 were disapproved for use in pesticide formulations.

Generally, such assessments are supported by research based on a wide variety of molecular mechanisms responsible for the effects of pesticides on their target organisms. In recent years, convicted organochlorine pesticides have been increasingly replaced by more effective and safer alternatives with faster biodegradation rates, such as organophosphorus pesticides and neonicotinoids pesticides. However, some of them can still affect the species that live in the waters, soil and tissues of contaminated plants that were not the objectives of the research. According to Campos [8], between 2019 and 2022, in Brazil, 2,181 new pesticide registrations were released, an average of 545 per year. However, it also describes that Brazil made an 87% jump in pesticide imports, from 384,501 tons in 2010 to 720,870 tons in 2021.

In view of these facts, it is important to recall the words of Professor Brian T. Newbold [9], in 1987, at the International Conference on Chemistry Education, in São Paulo, declared:

> "... Chemistry is the key to most of the major concerns on which the future of humanity depends, be they energy, pollution, natural resources, health or population. In fact, chemistry has become one of the components of the destiny of mankind. However, how many people, among the general public, know a little about the relevance of chemistry to the well-being of the world? It is essential that every citizen at least be made aware of the enormous contributions to modern life. ... We should not, however, ignore the negative aspects associated with chemistry-based progress, for to do so would be to close our eyes to reality [9].

It is the intention of this study to present and register the need to question the Teaching in the disciplines associated with Chemical Technologies, where the industrial processes must be unveiled and confronted based on the following points:

- On the assumptions and requirements of clean technologies;
- In the evaluations and knowledge of the chemical accidents that have occurred;
- Existing occupational and environmental liabilities;
- Sustainability and its broad aspect;
- In the quality of products that, directly or indirectly, converge to the broad definition of technologies that do not go against the grain of quality of life.

Hence the need to define the critical environmental view as the one that seeks to question the performance of certain activities, such as agriculture, mineral exploration, related industrial activities, considering their bias of the relationship between economic viability and sustainability in processing practices, which range from the exploration of raw materials to the final finished product. However, it is essential that man, life and the environment are present in this action and, finally, it is important that disinformation is always combated and never ignored.

On the other hand, the official environmental vision is linked to the current environmental legislation, regulated through laws, resolutions, regulations and decrees, which aim to establish rules for the implementation, operation, and inspection of enterprises. Based on the legislation, fines or reparations may also be applied to the conduct of any citizens or companies in relation to the environment. By means of these legal provisions, it is possible to punish offenders who harm the environment [10-14].

CRITICAL VIEW OF INDUSTRIAL PROCESSES AND THE ENVIRONMENT

The following are examples of some industrial processes that impact the environment and serve as directives or premises for the teaching of chemical technologies associated with environmental contamination.

AGRICULTURE AND THE ENVIRONMENT

World agriculture is based on several methodologies, ranging from the most archaic to the most modern technologies. In this way, many factors have determined the influence of man and agriculture on the environment.

Deforestation, as shown in Figure 2 [15-20], directly points to the increase in planting areas based on large-scale agriculture, which leads to environmental problems and localized climate change.

Figure 2 - Deforestation associated with agriculture

Sources: A: Korman [19]; B: Hamlett [20].

Another point that deserves to be highlighted is the chemical inputs, represented by the fertilizers used based on the percentage ratios of NPK that are related to chemical technologies. The element nitrogen (N) can be represented by the nitrogenous products, such as: ammonium nitrate (NH_4NO_3), sodium nitrate ($NaNO_3$), ammonium chloride (NH_4Cl), calcium cyanamide ($CaCN_2$), urea (CON_2H_4), etc. The element phosphorus (P) can be represented by sodium phosphate (Na_3PO_4), calcium superphosphates ($CaH_4P_2O_8$), mono ammonium phosphate ($NH_4H_2PO_4$), etc. The element potassium (K) is usually represented by potassium chloride (KCl) and potassium nitrate KNO_3).

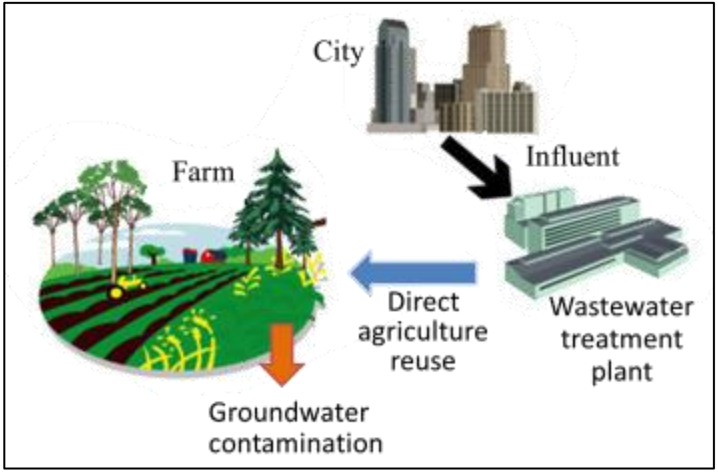
As seen earlier, sulfuric acid is the main raw material for the manufacture of phosphate fertilizers. The derailments of trains carrying sulphuric acid [3-6] and the aforementioned leaks constitute the dimension of the environmental problem.

NPK fertilizer formulations quantitatively represent the relationships of each specific chemical to plant species and soil types. The disposal of these products in the environment, mainly through irrigation, can also characterize environmental problems [21-25].

The use of direct agriculture reuse in the irrigation of agricultural areas, as shown in Figure 3, also deserves to be highlighted.

Next, the advantages and disadvantages of this technology are discussed considering the possible contamination of agricultural products and groundwater [26-28].

Figure 3 - Scheme of direct reuse water use in agriculture



Junior *et al*.[26] report that the application of reused water in a maize plantation resulted in a reduction in production costs and an increase in the productivity of the maize crop.

Research developed by Shakir *et al*. [27] describe that the use of wastewater from the effluent treatment plant with high salinity produces contamination in the plantations, making its use unfeasible.

The studies by Hajjami *et al.* [28] carried out in Morocco aimed to assess the potential risk of exposure to humans and animals when wastewater (raw and treated) was reused for irrigation of mint, coriander, alfalfa and cereal. In the microbiological examinations carried out on these agricultural products, helminth eggs (Taenia and Ascaris) were found, indicating that this technique is at odds with the health of the population that eats these foods.

In large-scale agriculture, or in a monoculture aimed directly at industrialization, the use of pesticides and fertilizers has been constant, and the results often reflect serious problems in the environment. As an example, the indiscriminate use of various types of pesticides that has caused contamination in millions of people and thousands of deaths per year worldwide [29 – 33].

Currently, about 100,000 crop protection formulas based on 1,500 active chemicals are being used in the most diverse parts of the world. When using pesticides, based on various methodologies, aiming to increase productivity, it is clear that a portion of these chemical formulations is adsorbed or absorbed in plants, while the other is incorporated into the soil, which can reach the groundwater with irreparable damage.

Figure 4 [34], below, shows photos of diseases and deformities associated with the use of pesticides used in India. The aspects of these photographs depict the suffering of innocent children who are contaminated with various products manufactured by uncompromised industries such as the environment and human beings.

Figure 4 – Pesticide associated diseases in India

Source: Caton & Lopez [34].

BAUXITE EXTRACTION IN ALUMINA PRODUCTION AND THE ENVIRONMENT

Also, in the same direction as environmental contamination, the media has shown that the exploitation of bauxite and the obtaining of high purity alumina from bauxite have led to leaks of red muds that impact the environment.

Most bauxites, which are economically usable, have an alumina content (Al_2O_3) between 50 and 55% and the minimum content for it to be usable is around 30%. About 40% of the bauxite produced in the world comes from Australia. The rest of the reserves are distributed among Guinea, Guyana, Jamaica, Brazil, India and China.

About 90% of the bauxite is converted into alumina for the production of aluminum, while the rest is distributed to refractory, cement, abrasives, etc. industries.

The panel in Figure 5 [35-38], below, shows the exploitation of bauxite advancing towards the forests, however, it is important to report that in order to minimize this action, some reforestation programs [39-41] have been carried out with the aim of mitigating this situation in view of the environmental assumptions.

Figure 5 – Bauxite ore exploration in Jamaica [A], Australia [B], Malaysia [C] and India [D].

Sources: A: The Jamaica Observer[35]; B: Batini [36]; C: The Star [37] ; D: Das & Padel [38].

According to the research of Balestrin *et al.* [39] It is essential to restoration areas destroyed after bauxite mining in order to keep the forest and its ecosystems active, as active restoration achieves a high accumulation of carbon (~ 58 mg/ha).

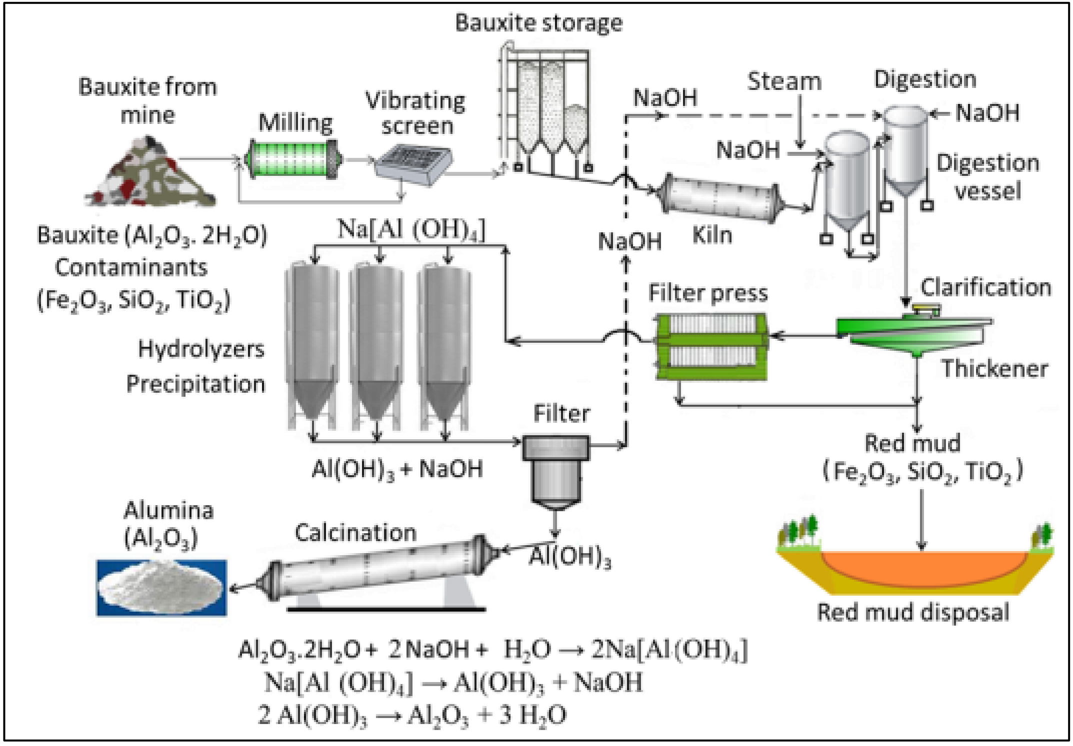
According to Lewis & Rosales [40], reports of bauxite mining in Guyana that resulted in deforestation and soil degradation are unknown and very similar to those of other bauxite-producing countries in South America. These facts show the need for research aimed at the knowledge of these degraded lands and the need for programs to restore these ecosystems.

Research conducted by Martins *et al.* [41] showed that the planting of several species after 8 years was quite satisfactory in the areas degraded by bauxite mining in the Eastern Amazon. The soil management methods, which included subsoiling and liming, were efficient in accelerating the recovery of degraded areas.

Figure 6 below shows the flowchart of the process of obtaining alumina (Al_2O_3) from the mineral bauxite to the disposal of red mud in red mud disposal and red muds dams. tailings reservoirs or waste dams.

The process of producing alumina (Bayer Process) from bauxite ore was patented on August 3, 1887 by chemist Karl Josef Bayer (1847-1904). According to Zhou *et al.* [42] World alumina production, in 2021, was 135 million tons while the discarded red sludge reached a value of 200 million tons, leaving deep environmental scars.

Figure 6 – Process flow diagram of alumina production



This proposed process, as shown in Figure 6, consists of the following steps:

- Grinding and sifting of raw bauxite in order to adjust the particle size to the process conditions;
- Digestion of bauxite in digesting vessels with steam and sodium hydroxide (NaOH), at a temperature of 200 ºC to 240 ºC and at a pressure of 20 to 30 atm., represented by the reaction:

$$Al_2O_3.2H_2O\ (s) + 2\ NaOH\ (\ell) + H_2O\ (g) \rightarrow 2\ Na[Al(OH)_4]\ (\ell);$$

- Clarification with thickener and filter to separate red sludge from soluble sodium aluminate - $Na[Al(OH)_4]$;
- The aluminate flows into hydrolysers where precipitation occurs in the form of aluminum hydroxide depending on the reaction:

$$Na[Al(OH)_4]\ (\ell) \rightarrow Al(OH)_3\ (s) + NaOH\ (\ell)\ ;$$

- Filtration and calcination in rotary kiln (200°C - 300°C) of aluminum hydroxide depending on the reaction:

$$2\ Al(OH)_3\ (s) \rightarrow Al_2O_3\ (s) + 3\ H_2O\ (g)$$

- Depending on processing and filtration, the alumina produced can be up to 99.9% pure;
- The recovered NaOH that comes out of the filters returns to bauxite digestion;
- The red mud that comes out of the thickeners is sent to the red mud disposal.

Figure 7 shows a panel of photographs of red mud leaks coming from companies producing alumina from bauxite.

Figure 7 – Toxic red mud from alumina processing leaks and contaminates rivers and cities [A] and [B] Brazil and [C] and [D] Hungary.

Source: A: Rodrigues [43]; B: Marchao [44]; C:NBC News [45]; D :Williams [46].

RESEARCH AND DEVELOPMENT OF METAL RECOVERIES FROM RED SLUDGE DEPOSITED OR IMPOUNDED IN RED MUD DAMS

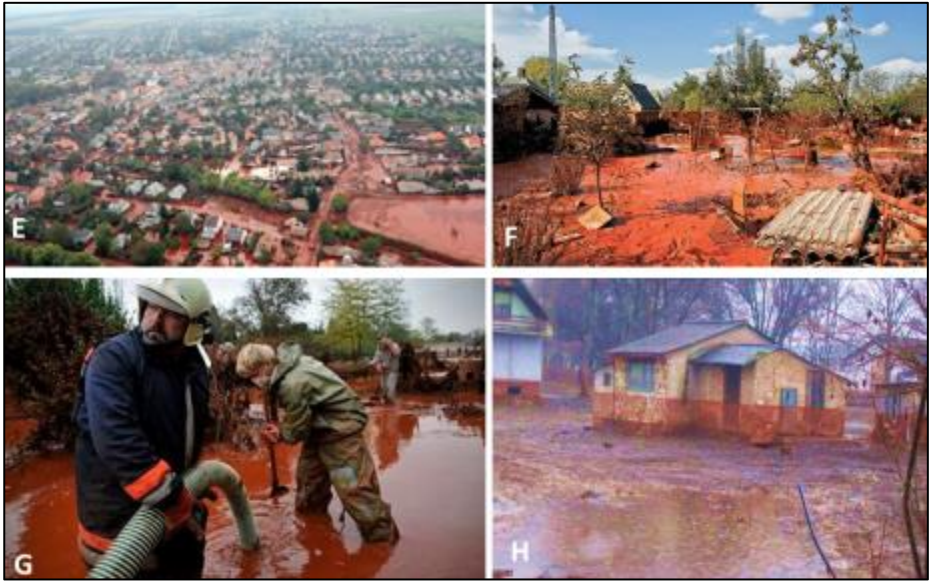
Currently, there is no doubt that there is a policy of gradual reduction of the red mud generated in the alumina production processes and, at the same time, there has been an increase in the concern and environmental expectation of companies and organized societies with the large mass of red mud deposited in the red mud dams over all these years. According to Zhou *et al.* [42] Many researchers have been working to obtain more efficient technologies to produce an eco-friendly red mud or to reduce the discharge of original red mud during the alumina extraction process. Other researchers have sought to make use of bauxite feasible or to develop innovative processes proposing the recovery of base metals such as iron, aluminum and titanium, rare metals and precious metals existing in the red mud.

However, what to do when a large reservoir of red mud collapses and floods an area of 40 km2, encompassing the towns of Devecser, Kolontar and Somlovasarhely in Hungary? Figure 7C

[45], Figure 7D [46], and Figure 8 [47-50] attest to how about one million cubic meters of toxic red mud affected life in cities.

The leakage of this red mud with high alkalinity (pH between 10 and 12), coming from this alumina production unit, resulted in great environmental degradation and, in this disastrous action, 200 people were injured and 10 died. Unfortunately, it was only possible to attend to the injured and rebuild the degraded areas.

Figure 8 – Red mud reservoir collapse floods city in Hungary



Source: E: The Sydney Morning Herald [47]; F :Everts [48]; G:Jahn et al. [49]; H:Thorpe[50].

The chemical compositions of these red sludges depend on the mining regions, geological formations and operating conditions of each industry that generates the red sludge. In the percentage scale of bauxite, the main impurities are Fe_2O_3, SiO_2 and TiO_2 and in the ppm scale (parts per million) the elements gallium, vanadium, manganese, chromium, scandium, yttrium, tungsten, etc. stand out.

Based on the educational focus of developing knowledge in chemical processes, some innovative technological research aimed at the recovery of iron and scandium in red sludge is selected and discussed below.

Iron recovery in red sludge

Table 1 below shows the levels of the elements Fe, Al, Si, Ti, Ca and Na and Table 2 shows the trace elements found in several red sludges with high alkalinity (pH 10-13) based on research by Liu & Naidu [51].

Table 1 - Concentration of major elements found in various red mud

Major elements	Concentration (%)
Iron	4.52 -50.6
Aluminum	4.42-16.06
Silicon	2.16-14.86
Sodium	0.98-7.79
Calcium	0.39-16.72
Titanium	0.98-5.34

Source: Liu & Naidu [51].

Table 2 - Concentration of minor elements found in various red mud

Minor elements	Concentration (mg/kg)
Gallium (Ga)	60-80
Scandium (Sc)	60-120
Yttrium (Y)	60-150
Manganese (Mn)	85
Chromium (Cr)	497
Vanadium (V)	730
Zirconium (Zr)	1230

Source: Liu & Naidu [51].

In the view of Pan *et al*.[52], it is essential to develop efficient technologies, with economic and industrial viability, with low energy consumption and zero secondary pollution, directed to red sludge in bauxite processing in order to reduce the red sludge itself and recover common, precious and rare metals.

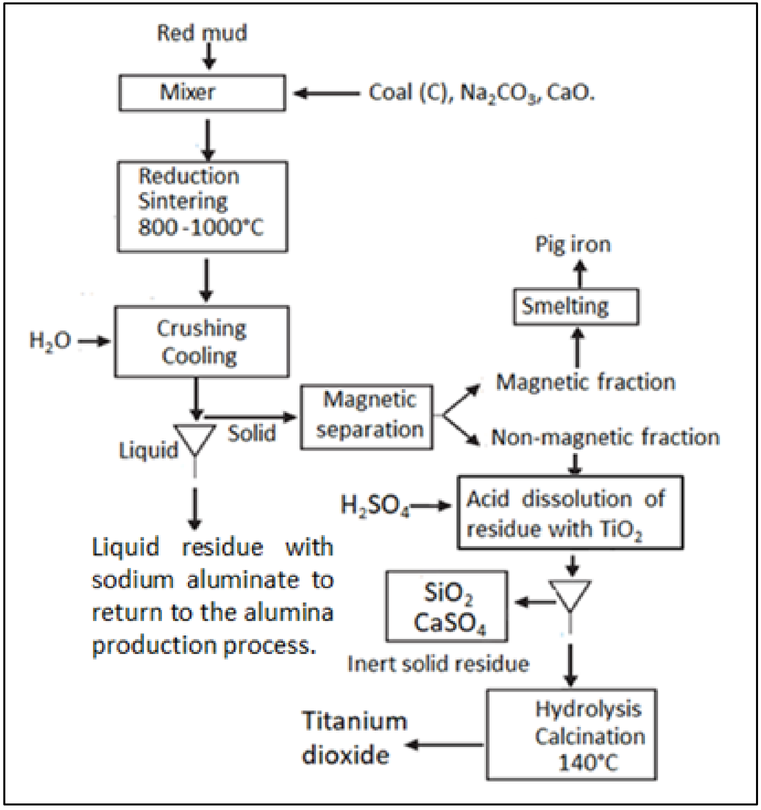
Regarding the use of iron in the solid molten form (small ingots), it will only be viable if the iron contents are high and the iron element is in the form of iron oxides that can be reduced and/or sintered to metallic iron to be used in the manufacture of cast iron or steels.

The pyrometallurgical recovery of iron present in red mud is one of the most investigated processes in the literature consulted. The simplified flowchart presented in Figure 9 below represents the combination of several techniques based on net mass reduction, thermal reduction, magnetic separation, among others, based on the referenced articles [51, 53-56].

This proposed process, as shown in Figure 9, includes the following steps:

- Wet red mud, in order to be industrially viable, the iron content in the ores must be greater than 60 wt. %;
- The iron-containing ores are: Hematite (α-Fe_2O_3), Goethite (α-FeOOH), Magnetite (Fe_3O_4) and Ilmenite ($FeO.TiO_2$).;
- Mixer o reduce and sinter the red mud, percentages are added in relation to the content of iron, coke (C), sodium carbonate (Na_2CO_3) and calcium oxide (CaO);

Figure 9 - Simplified flow diagram for pig iron production from red mud with high iron content.



- The addition of sodium carbonate (Na_2CO_3) in the red mud aims to increase alkalinity by promoting the formation of sodium aluminate which is entirely soluble, that is, avoiding the precipitation of aluminum hydroxide and aluminum oxide (Al_2O_3);
- The various reduction reactions that occurred in the reduction step (800 °C – 1000 °C) with the ferrous mineralogical species [57] present in the red mud are:

$$3\,Fe_2O_3\,(s) + C\,(s) \rightarrow 2\,Fe_3O_4\,(s) + CO\,(g)$$

$$3\,Fe_2O_3\,(s) + CO\,(g) \rightarrow 2Fe_3O_4\,(s) + CO_2\,(g)$$

$$Fe_2O_3\,(s) + 3\,C(s) \rightarrow 2\,Fe\,(\ell) + 3\,CO\,(g)$$

$$Fe_3O_4\,(s) + CO\,(g) \rightarrow 3\,FeO\,(s) + CO_2\,(g)$$

$$FeO\,(s) + CO\,(g) \rightarrow Fe\,(\ell) + CO_2\,(g)$$

- The magnetic separator separates the magnetic material from the non-magnetic material. The magnetic material rich in metallic iron goes into the melting furnace to produce the pig iron.
- The non-magnetic, ilmenite-rich material (($FeO.TiO_2$) will be processed to form titanium dioxide (TiO_2).

- The liquid waste, rich in sodium alumininate with pH ranging between 10 -13 returns to the alumina production process.

On the other hand, several researchers have developed studies using sulfuric acid in hydrometallurgical recovery to recover iron and other elements existing in red mud, although pyrometallurgical processes for iron are the most used [58,59].

Recovery of scandium and scandium oxide in red sludge

According to Yagmurlu *et al.* [60] and Riva *et al.* [61] Scandium is currently a valuable and important metal in a number of industrial sectors. However, despite its high price tag, the demand for scandium is increasing worldwide due to recent developments in a wide range of promising applications. The new aluminum-scandium alloys are primarily aimed at the aeronautical and transportation industries, sports equipment, and military demand. As an example, special scandium alloys have been used in primary satellite structures, cryogenic tanks, solar panel substrates, rocket nozzles and thrusters. Scandium is light weight, has higher thermal resistance and high mechanical strength. Compared to aluminum, the melting point of aluminum is 660.2°C while the melting point of scandium is 1540°C.

Scandium oxide (Sc_2O_3) powder is used in electronics, laser and superconducting materials, alloy additives, fuel cells, and various cathodic coating additives.

Considering the various degrees of purity of scandium (Sc 90% to 99.999 %) the price can range from US$ 5000 to US$ 15000 per kilogram, while scandium oxide (Sc_2O_3) depending on its purity can range from US$ 3000 to US$ 7000 per kilogram.

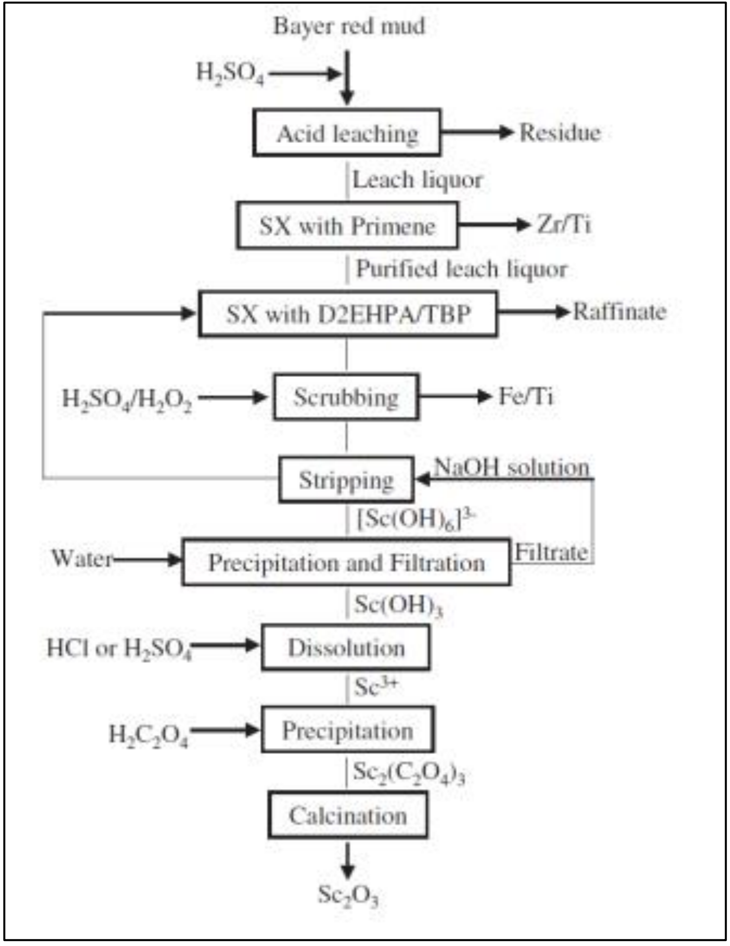
According to Ding *et al*. [62,63], scandium in nature is widely dispersed in various silicate minerals and rarely forms a major mineral deposit relative to its mineral concentration. This makes it complicated and impractical to extract scandium from raw ore with complex composition and extremely low grades. Therefore, it will be supplied mainly from the recovery of scandium from secondary sources such as red sludge from alumina production plants. Table 2 shows that the concentration of scandium is 60 to 120 mg/kg of red mud from alumina production plants.

As previously mentioned, red mud has become a source of scandium based on hydrometallurgical recovery . Considering the scarcity of scandium as a mineral source and the high cost of scandium and/or scandium-oxide, several studies have been proposed for this purpose [62-69]. The main researches are centered on leaching with sulfuric acid followed by extraction of specific organic solvents; calcination, acid leaching and recovery with ion exchange resins, among others.

The hydrometallurgical recovery process proposed by Wang *et al*. [64] It is presented in the simplified flowchart, below, in Figure 10, with the following steps:

- The red mud is leached with diluted sulphuric acid and the insoluble waste is filtered and discarded.
- The filtered solution is first treated with Primene JMT extractant to extract titanium and zirconium. Then, the extraction of the scandium from the other metals is existing in the solution is made with the extractant D2EHPA (di-2-ethylhexyl phosphoric acid);
- In Scrubbing, an H_2SO_4 and H_2O_2 solution is injected to eliminate the presence of Fe^{3+} and Ti^{4+} ions in the solution;
- Concentrated solution of NaOH is applied to remove the scandium in an aqueous solution, which is diluted to precipitate the scandium as $Sc(OH)_3$ concentrate;

Figure 10 - Flowsheet for scandium recovery from red mud.



Source: Wang et al. [64]

- $Sc(OH)_3$ is attacked by the HCl solution forming soluble scandium chloride as shown in the reaction:

$$Sc(OH)_3\ (s) + 3HCl(\ell) \rightarrow ScCl_3\ (\ell) + 3\ H_2O\ (\ell);$$

- Next, oxalic acid ($H_2C_2O_4$) reacts with $ScCl_3$ precipitating scandium oxalate - $Sc_2(C_2O_4)_3$ - which, when calcined, produces scandium oxide according to the reactions:

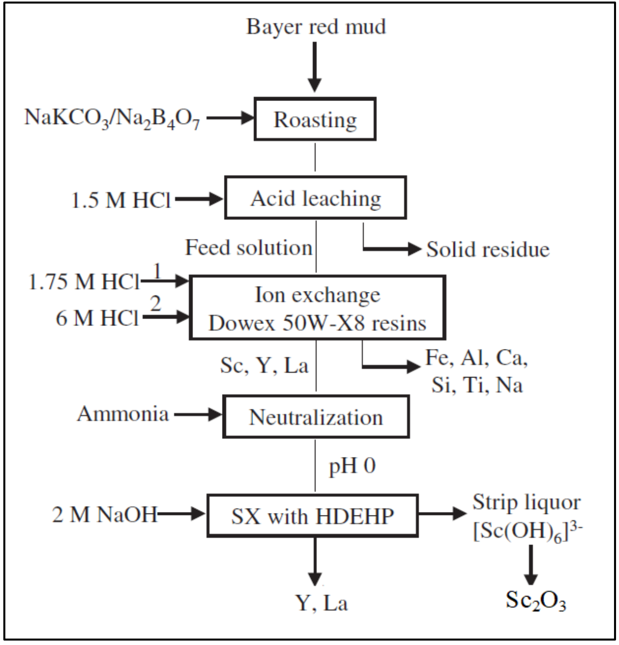
$$2\ ScCl_3\ (s) + 3\ H_2C_2O_4\ (\ell) \rightarrow Sc_2(C_2O_4)_3 + 6\ HCl\ (\ell)$$

$$Sc_2(C_2O_4)_3\ (s) \rightarrow Sc_2O_3\ (s) + 3\ CO_2\ (g) + 3\ CO(g)\ ;$$

Another process evaluated on the basis of hydrometallurgical recovery is proposed by Ochsenkühn-Petropulu *et al*. [65, 55] is presented in the simplified flowchart below, in Figure 11, consisting of the following steps:

- The red sludge is mixed with $NaKCO_3$ and $Na_2B_4O_7$ and introduced into the rosting at a temperature of 1100°C for 20 minutes. The sintered residue is then solubilized with 1.5 M HCl. The leached acid solution is sent to the ion exchanger resins and the insoluble solid residue is discarded;
- The Dowex-X8 ion exchanger resin recovers the Sc^{3+}, Y^{3+} and La^{3+} ions from the acid solution while the other ions are discarded;

Figure 11 - A flow diagram of scandiun oxide recovery from red mud.



Source: Ochsenkühn-Petropulu et al.,[66]; Liu & Li [68].

- The solution rich in Sc^{3+}, Y^{3+} and La^{3+} ions is neutralized with ammonia and the Y^{3+} and La^{3+} ions are extracted with the solvent di-(2-ethylhexyl) phosphoric acid (*HDEHP), while the* Sc^{3+} *ions are released in the form of* $[Sc(OH)_6]^{3-}$;
- The $[Sc(OH)_6]^{3-}$ rich solution is acidified to form scandium hydroxide, which is then calcined and transformed into scandium oxide based on the following reactions:

$$[Sc(OH)_6]^{3-} \rightarrow Sc(OH)_3\ (s) + 3\ OH^-$$

$$2\ Sc(OH)_3\ (s) \rightarrow Sc_2O_3 + 3\ H_2O\ (g).$$

- The recovered Y^{3+} and La^{3+} ion-rich solution is usually neutralized with NaOH and arranged in the form of Y_2O_3 and La_2O_3 oxides.

Scandium and its special alloys have been used in various projects, equipment and slides aimed at the aeronautical and aerospace industries. For industrial purposes, the purity of scandium ranges from Sc 99.9 %, Sc 99.999 %. The higher the purity of the metal, the higher the cost and consequently numerous refining processes will be required. The main raw material is scandium oxide ((Sc_2O_3) and its purity depends on recovery processes and secondary sources.

Table 3 below shows the levels of contaminants present in scandium oxides used as raw material standards in obtaining metallic scandium [70].

Table 3 - Technical requirements for scandium oxide

Indicator name	Norm	
	Sc_2O_3 99.9	Sc_2O_3 99.0
Outward appearance	White	White
Sc_2O_3, content, however, %	99.9	99.0
Impurities, calculated as oxide, however, %	0.005	--
Iron (Fe_2O_3), %	0.003	0.05
Aluminum, (Al_2O_3), %	0.01	0.01
Calcium (CaO), %	0.03	0.05
Copper (CuO), zirconium (ZrO_2), %	0.01	0.01
Silica (SiO_2),%	0.03	0.05
Manganese (MnO_2), magnesium (MgO), %	0.005	0.05
Yttrium(Y_2O_3), Ytterbium (Yb_2O_3), %	0.01	0.05
Phosphorus (P_2O_5), %		0.02

Source: Mukhachov et al.[70]

Scandium can be obtained directly from the calciothermic reduction of Sc_2O_3 with metallic calcium or from the conversion of Sc_2O_3 to scandium fluoride (ScF_3) through direct reaction with hydrogen fluoride (HF) gas followed by calcium-thermal reduction.

The calcium-thermal reduction of scandium oxide is carried out at 1000°C in a crucible tantalum, according to the following reaction:

$$Sc_2O_3(s) + 3\ Ca\ (g) \rightarrow Sc\ (s) + CaO\ (s)$$

The attainment of scandium by Fluorination It consists of two phases: the first comprises the attack of Sc_2O_3 with hydrogen fluoride at 500°C to form scandum fluoride. Subsequently, the scandium fluoride reacts with calcium at a temperature of 1600 °C, according to the reactions:

$$Sc_2O_3\,(s) + 6\,HF\,(g) \rightarrow 2\,ScF_3\,(s) + 3\,H_2O\,(g)$$

$$2\,ScF_3\,(s) + 3\,Ca\,(g) \rightarrow 2\,Sc\,(s) + CaF_2\,(s)$$

Scandium can also be obtained by the high-temperature electrolytic process using molten scandium oxide or fused scandium fluoride as an electrolyte. The process consists of the use of a solid oxide cathode consisting of Sc_2O_3, aiming at the production of scandium that is introduced into an electrolytic cell containing a $CaCl_2$ molten electrolyte based and can solubilize the Sc_2O_3 at a temperature of about 900 °C. The oxide ions released during the cathode reaction will diffuse in the molten salt electrolyte, being then discharged at the anode.. The electrolytic reaction produces oxygen in the graphite anode (C) which, at a temperature of 900°C, when reacting with carbon, generates CO_2. However, the processes are more complex when the purity of scandium is desired [70-75].

Cathode, anodic, and total reactions are presented below:

$$\text{Cathodic reaction: } Sc_2O_3\,(s) + 6\,e^- \rightarrow 2\,Sc\,(s) + 3\,O^{2-} - ;$$

$$\text{Anodic result: } 2\,O^{2-} + C\,(s) \rightarrow CO_2\,(g) + 4\,e^- ;$$

$$\text{Total cell reaction: } 2\,Sc_2O_3\,(s) + 3\,(s) \rightarrow 4\,Sc\,(s) + 3\,CO_2\,(g)$$

It is important to emphasize that the processes presented are part of a policy to recover industrial waste that is not contrary to environmental sustainability, preserving man and the environment.

THE DIFFERENT FACES OF CARBON DIOXIDE (CO2) IN THE INDUSTRIAL SYSTEM AND THE ENVIRONMENT

Carbon dioxide (CO_2) is known in three forms, the first as an important raw material in the production, directly or indirectly, of various products that provide a number of advantages in the production of goods for humanity. However, at the other end of the spectrum, CO_2 appears as a villain, whether of the environment, as a cause of the warming of the globe, or when dissociated in water and salt spray it becomes a corrosive agent to industrial equipment [76].

On an industrial scale, CO_2 is produced to meet the needs of various segments, being supplied in gaseous, liquid and solid form. It is used in the manufacture, directly or indirectly, of various products, such as, soda ash (Na_2CO_3), salicylic acid (drug), urea (fertilizer), methanol, carbonating of soft drinks and mineral water, refrigeration and preservation of food products, fire extinguishers charges (CO_2), neutralization of acid effluents, and so on.

The origin of the raw materials and the various industrial technologies adopted in the manufacture of carbon dioxide, as well as the recovery of gases from a chimney or other origins, are fundamental factors that dictate the quality of the final product. The level and type of contaminant are inseparably linked to its origins and the processes imposed.

CO_2, on an industrial scale, can be classified in two forms: the first as a primary production and the second as a secondary or residual source.

Primary sources

Examples of primary sources include the calcination of limestone ($CaCO_3$) in cement plants or the burning of natural gas (methane – CH_4) in electric power generators, as shown in the following reactions:

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$$

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2 + 2\ H_2O\ (g)$$

The contaminants present are directly related to the origin of the raw materials. In the specific case of limestone, if it has iron sulfide (FeS) as a contaminant, it is possible that the final product will be contaminated as sulfur dioxide (SO_2) depending on the reaction:

$$FeS\ (s) + 3/2\ O_2\ (g) \rightarrow FeO\ (s) + SO_2\ (g)$$

In the case of methane, the contaminant, hydrogen sulfide (H_2S), is common, whose burning is also transformed into SO_2 according to the reaction:

$$H_2S\ (g) + 3/2\ O_2\ (g) \rightarrow H_2O(g) + SO_2(g)$$

Secondary sources

The following are some examples of secondary sources with their respective contamination considerations:

1) Gases from the Steam Reform Process [77] of hydrocarbons aiming at the production of hydrogen and CO_2 consists, essentially, of the reaction of a hydrocarbon, such as natural gas, with steam, in the presence of nickel catalysts and at a temperature of 870 °C. The reactions of the process are presented below:

$$CH_4\ (g) + H_2O\ (steam) \rightarrow CO(g) + 3\ H_2(g)$$

$$CO\ (g)\ +\ H_2O\ (steam) \rightarrow CO_2\ (g)\ +\ H_2(g)$$

The separation of CO_2 from hydrogen H_2) is done through absorption and regeneration in monoethanolamine (MEA) towers, which enables the contamination of MEA in the final product, requiring new contaminant removal processes.

2) Gases from the burning of fuels in furnaces and boilers

Fuel oils and other fossil fuels used in boilers and furnaces generally contain sulfur compounds in the form of H_2S (hydrogen sulfide), R-SH (mercaptans), R-S-R (organic sulfide), R-S-S-R (organic disulfide), which when burned with air generate SO_2 and SO_3, respectively, in the proportion of 90 and 10%. Nitrogenous compounds, on the other hand, depending on their chemical function and burning conditions, can form N_2 and NO_x (NO, N_2O, NO_2). This means that the production of good quality CO_2 justifies the need for an efficient system for the removal of these contaminants.

3) Carbon dioxide from fermentation industries

The CO_2 stream from the fermentation industries (sugar/alcohol) generally provides a carbon dioxide of excellent quality, although an absorption system is necessary to remove some contaminants that accompany fermentation processing, such as traces of alcohol, acetone and acetic acid. This is one of the most reliable processes in terms of quality, in view of the origin and knowledge of the raw materials used and the processes involved.

The quality of CO_2 for use in the carbonating of soft drinks and mineral water

To exemplify a parameter for teaching chemical technology, the quality of CO_2 for use in the gasification of soft drinks and mineral water can be highlighted, based on Table 3, referring to the levels of contaminants allowed for this purpose.

According Steen & Ashurst [77], as shown in Table 3, this is a minimum standard that all carbon dioxide needs to be delivered to manufacturers of soft drinks and carbonated mineral water. It is essential that all CO_2 supplies for this purpose must have certificates of conformance for each specific batch. On the other hand, the user should take great care when using carbon dioxide to ensure that it is fit for purpose. The supply chain must be regularly audited, including the actual carbon dioxide manufacturing plant, storage and distribution to site.

Another point that should be highlighted is the levels of some toxic contaminants, such as methanol, phosphine, hydrogen cyanide, benzene and carbon monoxide that may be present in CO_2. In addition, depending on the carbon dioxide production method as presented above, the certificate of conformance must include analytical checks for each batch produced, as well as the identification of the process and the origins of the raw materials.

Table 3 - Commodity specification for carbon dioxide

Component	Concentration
Assay	99.9% v/v, min.
Ammonia	2.5 ppm, v/v, max;
Oxygen	30 ppm, v/v, max.
Oxides of nitrogen (NO/NO_2)	2.5 ppm, v/v, max. each
Non-volatile residue (particulates)	10 ppm, w/w, max.
Non-volatile organic residue (oil and grease)	5 ppm w/w, max.
Phosphene	≤ 0.3 ppm, v/v
Acetaldehyde	0.2 ppm, v/v, max.
Benzene	0.02 ppm ,v/v, max.
Carbon monoxide	10 ppm, v/v, max.
Methanol	10 ppm, v/v, max.
Hydrogen cyanide (HCN)	<0.5 ppm, v/v
Total sulphur (as sulphur)	0.1 ppm, v/v, max.
Taste and odour in water	No foreign taste or odour

Source: Steen & Ashurst [78]; AIGA [79].

The critical analysis based on Table 3 reveals that some contaminants are allowed due to the existing processes, however, depending on the production route of some processes can never be used for refrigerant gasification.

In this way, questioning is an important tool in the formation of critical technical awareness in the selection of processes and products.

THE DISCIPLINE OF CHEMICAL TECHNOLOGY

This means that the teaching of the discipline of Chemical Technology must be firmly linked to critical questioning, involving all stages of the industrial process, from the raw material to the final product. In addition, it is important to raise awareness and hold professionals accountable for the use of the product in the various segments of goods made available to society. These guidelines aim to reveal to the student a new dimension of chemical processes based on the advantages and disadvantages of these processes and products in relation to man and the environment [80].

Generally, the syllabus of these disciplines at the Brazilian University is composed of the following topics: classical and modern processes of the following products: sulfur and sulfuric acid barrel and caustic soda, chlorine and hydrochloric acid, ammonia, nitric acid, nitrogen fertilizers, phosphorus, phosphoric acid and phosphate fertilizers, potassium fertilizers; Industrial gases: oxygen, nitrogen, carbon dioxide and hydrogen.

These menus aim to:

- identify and characterize the various types of inorganic processes used to obtain chemical products, which in turn can be used in various industrial segments;
- recognize and establish the critical relationships between knowledge of chemical processes and the environment based on industrial contamination or wastewater treatments;

- Visualize and consolidate the vision of the present and the future based on the principles and guidelines of clean technologies.

Most of the processes included in the referenced menu were conceived at the beginning of the century or in the 1950s, where the principles of preservation of man, the environment and industrial safety were not fundamental requirements in the implementation of these large basic industries.

Currently, it is common to have at least three competitive technologies for the manufacture of the same classic inorganic product, however, depending on their use, it is essential to establish different criteria for each industrial process, for example, the criteria of a pharmaceutical industry are entirely different from those of the petrochemical industry. Therefore, it is important to define broad or detailed criteria for each industrial action.

Due to the quality and use of chemical products, as well as the possibility of chemical accidents in industrial processes, it is essential to make chemical professionals aware of the responsibility in the direct or indirect use of a chemical product and the related technologies of its production [80].

CONCLUSIONS

In view of the above facts, it is concluded that it is necessary to:

- to develop a technical-critical awareness in society, especially in the University, which aims at understanding the manufacturing routes of products and the contaminants generated and/or aggregated during industrial processing, with a view to product quality and environmental preservation;
- question and re-evaluate industrial processes based on environmental, social, occupational, economic and political parameters in order to develop a methodology for the evaluation and use of chemical products;
- To develop in students, due to the quality and use of chemical products, the responsibility to produce and indicate the use of these products in other industrial segments.

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