The Use of Cadmium in Industrial Segments Leaves a Trail of Contaminations in Humans, Health and the Environment

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The Use of Cadmium in Industrial Segments Leaves a Trail of Contaminations in the Environment

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ABSTRACT

?Cadmium is produced from by-products of the mining, smelting and refining of zinc sulfide (ZnS) ores and, to a lesser extent, lead and copper ores. Cadmium minerals (greenockite - CdS) do not occur in sufficient concentrations and quantities to justify their extraction and processing.The element cadmium?object of this study was chosen because it is present, directly or indirectly, in several industrial segments and at the same time because it is considered an element extremely toxic, bioaccumulativeand currently occupying the seventh place among the toxic substances with the highest risk of causing harm to humans.In this study, the industrial production of cadmium metal, electrolytic refining, cadmium metal purity, Nickel-Cadmium batteries,the manufacture of cadmium alloys, pigments, the cadmium electrolytic deposition process and the effluent treatment processes containing cadmium ions (Cd^{2+}) are discussed.In addition, the experiments are presented to show how the identification of the element cadmium was conducted in the past, the galvanic series of cadmium, contaminations during welding of silver-cadmium alloys and the deposition of cadmium in carbon steel.Finally, the conclusions are focus on the critical view of the use of cadmium in the several industrial segments and its toxicity.

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Note: An abstract summarizes, usually in one paragraph of 300 words or less, and commonly has: introduction, purpose, method, result, and conclusion. Please follow this guidance!!!!!

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Keywords:cadmium, nickel-cadmium batteries, contaminations, cadmium coatings, cadmium effluents

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1. INTRODUCTION

In the last three decades, due to the high contamination of toxic metals and semimetals present on the planet,the world's conscience has been consolidating the need to readapt and/or modify the industrial processes, products and

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equipment resulting from these industrializations in order to preserve man, public health and the environment.

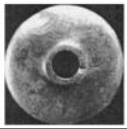
In the distant past, as in the Roman Empire, several artifacts used lead, copper and bronze (copper-tin alloys) that were manufactured in primitive foundry [1] that exhaled a large amount of toxic gases into the atmosphere without any environmental concern.

In the research and search for the history of ancient peoples, in the archaeological excavations carried out in the northern Negev Desert, Israel, archaeologists detected the presence of metals such as copper, lead, tin, silver and semimetals such as arsenic and antimony present in the slag from primitive furnaces and also in metallic artifacts as they show, respectively, Table 1 and Fig. 1.?

Table 1. Chemical composition of slag from primitive furnaces obtained in archaeological excavations

	Chemical Composition, %										
Sample	CuO	Fe_2O_3	Mg	Mn	S	Pb	Zn	SiO_2	As	Sb	Ni
SQ 1207	41·4	38·5	0·23	0·03	1·56	0·033	0·004	11·7	0·005	0·011	0·015
SQ 7354	34·0	44·3	0·20	0·01	2·30	0·077	0·002	7·72	0·006	0·007	0·015
SQ B·70	48·9	16·5	0·15	0·01	1·73	0·022	0·001	17·9	0·004	0·009	0·055

Source: Golden *et al.* [2], modified



	Chemical Composition, %								
	Cu	Sb	As	Ag	Pb	Ni	Sn	S	Fe
Surface	80·4	11·7	3·66	0·85	0·21	0·15	0·11	0·12	0·06
Bulk	83·3	10·1	4·34	0·35	0·14	0·14	<0·001	0·08	0·02

Fig. 1. Chemical composition of disc-shaped artifacts discovered in archaeological excavations Source: Golden *et al.*[2], modified

The results of these chemical analyses show the contamination of the soil by these elements and lead to the conclusion that the health of the artisans, the metallurgists of that time, was probably greatly compromised during the processing of these archaeological alloys, which are currently part of museums in the form of objects [2,3].

Similarly, the metallic pigments and oxidized materials obtained from these artisanal operations were also used in paints for fresco paintings and in ceramic vases. The lead, arsenic and antimony found in these archaeological excavations show the degree of environmental contamination prevailing at that time[2,3].

Generally, these primitive manufacturing units such as foundries were located far from the cities to prevent the bad smell, the accumulation of garbage and the slag from being noticed by the population. With the growth of cities, such systems became closer and closer and to get rid of these problems, rulers transferred these polluting agencies further away.

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However, there comes a time when two or three peripheral cities, when expanding, end up totally involving that polluting unit. Today, what you see in a satellite image is a completely static factory surrounded by the city with all its problems. Where soil, air and water are often affected by contamination, eitherby lack of control or by lack of waste treatment. In this way, it is evident that the degradation of the environment in all aspects did not appear suddenly, but accumulated over a distant history.

The cadmium metal and/or its alloys, ?object of this study is hardly visible when compared to the metals and semimetals previously determined in the archaeological excavations particularized by the Roman Empire[?]. This fact is due to the fact that cadmium has practically no mineral deposits, it is usually found in small quantities and is associated with zinc deposits. At that time, mineral exploration was directed to copper and lead deposits. There are no historical notes of zinc exploration in these regions

However, cadmium appears in the form of natural orange pigments, derived from minerals identified as cadmium sulfoselenide (CdS.Se) when paint restorations of Ancient Greek terracotta artifacts belonging to the museum were carried out [4]. Research carried out by Bourdin *et al*. [5] on 34 ceramic fragments excavated from 6 archaeological sites in Ecuador and Ghana indicated the presence of cadmium in the form of natural pigments of yellowish color (cadmium sulfide, CdS).

These ancient vessels were used for food and these regions are rich in zinc deposits where cadmium is part of these ores[?]. The authors of this research seek to link cadmium to food contamination in ancient times.There are references that since the Middle Ages yellowish deposits (cadmium oxide, CdO) had already been observed in the chimneys of furnaces producing metallic zinc[?].

However, it was not until 1817 that the discovery of cadmium was observed as an impurity of zinc carbonate ($ZnCO_3$) identified by Friedrich Strohmeyer, Professor of Chemistry and Pharmacy at the University of Göttingen, Germany. Strohmeyer was experimenting with zinc carbonate, which is white, when he realized that heating produced a different yellow color than expected for the compound [6].

After more detailed studies, he concluded that the cause of the color change was the presence of an oxide of another, still unknown element, cadmium. Probably, cadmium sulfide (CdS) contaminated zinc carbonate and when they were heated to a certain temperature, zinc oxide (ZnO) was formed, which is white, and cadmium oxide (CdO), which is yellow, as shown in the following reactions:

$$ZnCO_3 \rightarrow ZnO + CO_2$$

$$CdS + 3/2\ O_2 \rightarrow CdO + SO_2$$

The name cadmium was given because it was extracted from “cadmia”, a designation used for the ore rich in zinc carbonate. At the same time, the discovery of cadmium was also attributed to Karl Samuel Leberecht Hermann who, upon examining zinc ingots from zinc smelting, observed a yellowish coloration (cadmium oxide, CdO) on their metallic surface, instead of the white coloration due to zinc oxide (ZnO) [6].

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The first industrial production of cadmium metal took place in Germany in the 19th century and until 1911 Germany was still the most important producer of cadmium ingots. Another fact that deserves to be noted is the cadmium industrial electrodeposition on carbon steel, where in 1940 (during World War II) it represented approximately 75% of the total consumption of cadmium, that is, about 3600 tons per year [6].

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Currently, the production of cadmium has been reduced due to its toxicity and the environmental problems that have affected man and the environment. Considering the facts previously described, the present study aims to evaluate the behavior of the element cadmium in the various industrial segments based on the following parts:

- Cadmium metal industrial production process, electrolytic refining and cadmium metal purity;
- Cadmium and its industrial applications;
- Cadmium electrolytic deposition process;
- Effluent treatment processes containing cadmium ions (Cd^{2+});
- Human exposure to cadmium;
- Examples of experiments showing the identification of the element cadmium, the galvanic series of cadmium, and the electrolytic deposition of cadmium in carbon steel.
- Conclusions.

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The Use of Cadmium in Industrial Segments Leaves a Trail of Contaminations in the Environment

2.CADMIUM METAL INDUSTRIAL PRODUCTION PROCESS, ELECTROLYTIC REFINING AND CADMIUM METAL PURITY

2.1.Industrial production of cadmium metal

Cadmium is a soft, malleable and ductile metal, silver-white in color. The melting point, boiling point and density are respectively 320.9°C, 765°C and 8.65 g/cm^3.

Cadmium can be considered a rare metal, as it is estimated to be in the order of 0.2 to 0.3 g/t in the Earth's crust. Its characteristic mineral is greenockite (CdS), and it is not found isolated, only associated and in small amounts with the minerals zinc, copper and lead. It is not considered a commercial mineral, because in sphalerite (ZnS), a zinc ore, it occurs in the proportion of 1 to 2 %.

In this way, the primary production of cadmium is designed for recovery using the gases and metal dusts from the roastings furnaces, from the pyrometallurgical process of zinc ores, fromcadmium residues from copper and lead smelting plants, from zinc collected in distillation into zinc retorts, and from the high-cadmium precipitate obtained in purifying zinc electrolyte at electrolytic zinc industrial plants[6,7].

2.1.1. Recovery of cadmium from the pyrometallurgical process for the production of zinc from zinc sulfide ores

The pyrometallurgical process using a sulfide ore concentrate containing 47 to 60 % zinc is shown in Fig. 2.It essentially consists of roasting and thermal reduction with coke (C) in the horizontal retort forming impure zinc. The temperature in roasting is in the order of 1000°C to 1200°C while the temperature in horizontal retort is 1400°C. During roasting, it is normal to volatilize 3 to 5% cadmium together with SO_2 and dust.

Finally, impure zinc metal is processed in fractional distillation where the temperature of 765°C-780°C is fixed for the separation of cadmium from zinc, considering that the boiling temperature of cadmium and zinc are, respectively, 765°C and 906°C. Overall, this process has a yield of 3 kg of recovered cadmium for one ton of zinc produced [6,7].

The reactions involved in this process are presented below:

$$ZnS + 3/2\ O_2 \rightarrow ZnO + SO_2$$

$$ZnO + C \rightarrow Zn + CO$$

$$ZnO + CO \rightarrow Zn + CO_2$$

$$CdS + 3/2\ O_2 \rightarrow CdO + SO_2$$

$$CdO + C \rightarrow Cd + CO$$

$$CdO + CO \rightarrow Cd + CO_2$$

Sulfur dioxide (SO_2) is recovered to form sulfuric acid whose reactions are presented below:

$$SO_2 + 1/2\ O_2 \rightarrow SO_3$$

$$SO_3 + H_2SO_4 \rightarrow H_2SO_4.SO_3$$

$$H_2SO_4.SO_3 + H_2O \rightarrow 2\ H_2SO_4$$

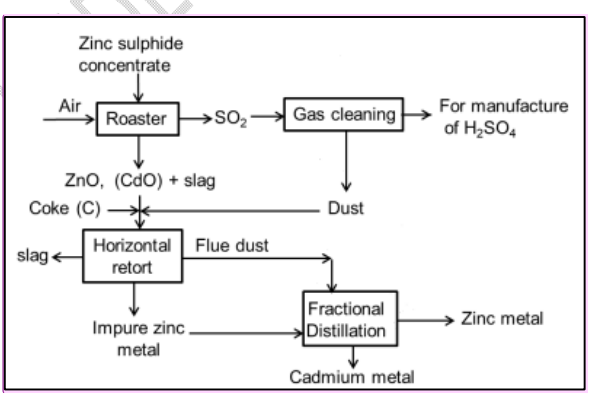

Fig.2. Simplified flowchart for obtaining zinc and cadmium by pyrometallurgical process

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2.1.2. Recovery of cadmium using sulfuric acid leaching of mineral residues and metal particulates from zinc and lead production furnaces

In leaching with sulfuric acid, sulfide mineral residues and dust and/or particulate material from retorts and furnaces can be used.

Sulfide residues containing CdS, PbS and ZnS must be roasted to form their characteristic oxides and prevent the release of hydrogen sulfide (H_2S) during acid attack as shown in the reaction below:

$$CdS + H_2SO_4 \rightarrow CdSO_4 + H_2S$$

The vaporized residues (dust and particulates) from the retorts are usually made up of cadmium oxide (CdO) and lead oxide (PbO).

The acid leaching process as shown in Fig. 3 essentially consists of the reaction of sulfuric acid with residues containing cadmium, zinc and lead and the resulting solution is filtered in a filter press. The precipitated lead sulfate ($PbSO_4$) and silica (SiO_2) are retained in the filter while the solution containing Zn^{2+} and Cd^{2+} in the form of soluble sulfate is sent to the precipitation tank to form the cadmium sponge through the addition of zinc.The cadmium sponge is then sent to the furnace to form cadmium metal and the zinc sulfate solution is sent to the electrolytic plant to produce zinc metal [6,7].

The reactions involved in acid leaching are presented below:

$$CdO + H_2SO_4 \rightarrow CdSO_4 + H_2O$$

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$$

The addition of zinc powder, preferentially, displaces the Cd^{2+} ions based on the electrochemical series where zinc has the potential of –0.76V and cadmium –0.40 V as shown in the reaction:

$$Cd^{2+} + Zn \rightarrow Zn^{2+} + Cd$$

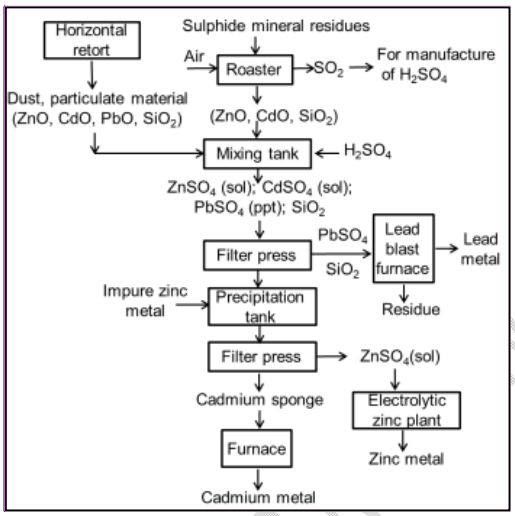

Fig. 3. Process for obtaining cadmium by acid leaching of retort and roasting residues, Source: Mentch&Lansche [6],modified.

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The recovery of cadmium is also obtained directly by fractional distillation of various residues originating from the manufacture of Cd-Ni batteries, cadmium-copper alloys, hot-dip galvanizing residues, among others, considering an obvious advantage, as cadmium is 12-18 times more expensive than zinc.

2.1.3. Cadmium Electrolytic Refining

Electrorefining and electrowinning both are electrolytic processes used to produce pure cadmium cathode sheet. In the former process, a cadmium electrolytic refining cell consisting of a slab of crude cadmium to be refined (anode) and a thin aluminum starting sheet (cathode) are immersed in an aqueous electrolyte, and direct current is passed through the cell.

The dissolved cadmium from the crude anode in the form of Cd^{2+} ions is redeposited on the cathode and the impurities are either deposited or dissolved in the electrolyte.

The electrochemical reactions below show the dissolution of the anode and the reposition of cadmium on the cathode (aluminum sheet). Aluminum sheet is used because of the ease for the removal of deposited cadmium plate.

Dissolution of the anode: $Cd - 2e^- \rightarrow Cd^{2+}$

Redeposition on the cathode: $Cd^{2+} \rightarrow Cd - 2e^-$

The formation of hydrogen (H_2) is due to the dissociation of the sulfuric acid present in the electrolyte according to the reaction:

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

$$2\,H^+ + 2\,e^- \rightarrow H_2$$

As shown in the schematic in Fig. 4, the solution is pumped from the cell and the impurities are removed by filters. Purified electrolyte is returned to the cell as catholyte and deposited on the cathode as pure cadmium. Electrowinning, also an electrolytic process, can electrolyze soluble anodes of cadmium sulfide (CdS) or utilize insoluble anodes to extract the cadmium from leach liquor [8-11].

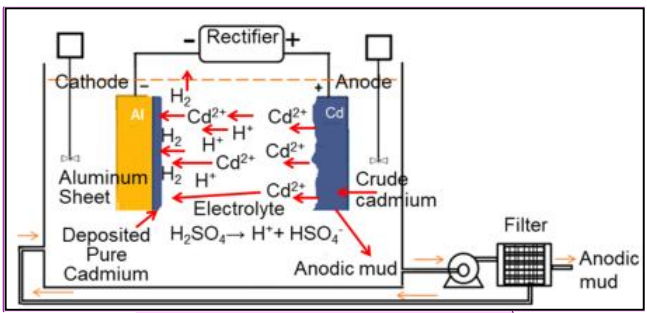

Fig.4. Cadmium electrolytic refining scheme

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The cadmium crude anode used in electrolytic refining usually originates from the melting of cadmium sponge, powder, residues and metal shavings, as shown in Fig. 5 below.

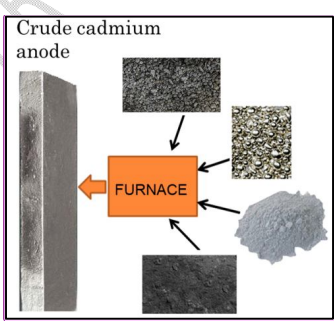

Fig. 5. Crude cadmium anode

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The literature is quite extensive and presents a diversity of operating conditions that can interfere with the efficiency of the process, such as: concentration of Cd^{2+} ions in the electrolyte, free sulfuric acid concentration, current density, temperature, voltage and additive additions to improve cadmium deposition on

the aluminum cathode. Table 1 presents some of these operational parameters of the cell.

Table 2. Operational parameters for the process of electroplating of cadmium

Operational parameters	Performance range
Concentration of Cd^{2+} ions in the electrolyte	50 a 150 g/L
Free sulfuric acid concentration,	10 a 150 g/L
Current density,	100 a 400 A/m^2
Temperature,	25 a 70ºC
Voltage	3 a 5 V

The process of electroplating metals is one of the simplest methods for the production of high purity metals, in the case of cadmium, the purity reaches 99.96%. However, purity often decreases when the electrolyte contains several metallic cations and co-deposition can occur at the cathode. Generally, Cu^{2+}, Ni^{2+}, $Pb^{2+}$and Zn^{2+} ions can interfere with and reduce the purity of metal cadmium.

Crude cadmium anode can contain precious metals, residues from slag, cadmium sponge, and even inorganic compounds such as cadmium sulfide (CdS). During electrochemical processing, as the cadmium anode dissolves into Cd^{2+}, an insoluble residue breaks off and forms anodic mud. The anodic mud insoluble in the acid electrolyte is retained in the filter and is removed for specific treatment.

Insoluble cadmium sulfide (CdS) can be transformed into soluble cadmium sulfate ($CdSO_4$) by adding hydrogen peroxide (H_2O_2) to the electrolyte as shown in the following reaction [15]:

$$CdS + 4\ H_2O_2 \rightarrow Cd^{2+} + SO_4^{2-} + 4\ H_2O$$

2.1.4.Obtaining High Purity Cadmium by Vacuum Distillation

Cadmium can be purified by vacuum distillation based on the evaporation and condensation technique used for low boiling and melting point materials to remove high melting point and low vapor pressure metal impurities at the ppm level. This technique can provide cadmium with a purity of 99.9999% with removal of the following impurities: Si, Ca, Fe, Ni, Cu, Zn, As, Se, Ag, Sb, Tl, Pb and Bi [12-15].

The relative volatility of cadmium and metallic and semi-metallic impurities with respect to the partial pressure of 10^{-3} atmospheres is shown in Table 3.

Table 3. Relative volatility of metals e semimetals

Metal/semimetal	Temperature (ºC), for partial pressure of 10^{-3} atmospheres
Cadmium	384
Arsenic	363
Zinc	477
Tellurium	509

Antimony	872
Lead	953
Bismuth	1008
Manganese	1269
Gallium	1329
Tin	1470

The schematic of the vacuum distillation unit presented in Fig. 6, developed by Munirathnam *et al.*[12] consisted, essentially, of two cylindrical crucibles (made up of isostatic fine grain high density graphite) inverted over one on the other. A copper cooling jacket was placed on top of the graphite crucible to act as a condenser.

The entire assembly was placed in a stainless steel retort (AISI 316L) connected to a vacuum system. This stainless steel retort was then placed in a heating oven with a temperature controller system within ± 5°C. The system was dynamically maintained at a vacuum of approximately 2 x 10^{-5} atmospheres before initiating evaporation of the molten metal and almost 2 x 10^{-4} atmospheres during the distillation process.

High purity cadmium (99.9999%) has been used in the manufacture of high purity compounds (CdTe, CdZnTe, HgCdTe, CdS, CdSe, etc.) for several industrial applications, such as: solar cells, IR detectors, imaging devices, electro-optical modulators, fluorescence, etc. [15].

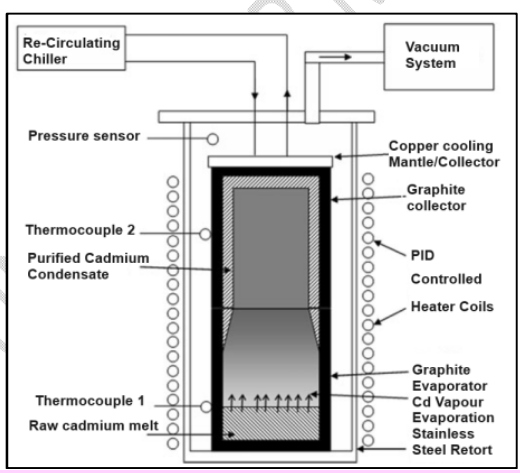

Fig. 6. Schematic diagram showing components vacuum distillation assembly Source: Munirathnam *et al.* [12]modified.

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2.1.5. Cadmium recovery using microorganisms and aquatic plants

The presence and accumulation of Cd^{2+} ions in municipal and industrial wastewater or in water from agricultural production can lead to the contamination of cadmium in human consumption products that are directly related to human health. Fungi, yeasts, algae, and aquatic plants can remove heavy metals from aqueous solutions in large quantities, all known as bioremediers [16].

Research developed Rehman& Sohail Anjum [17] show that *Candida tropicalis* was capable to remove 40 to 78% of the Cd^{2+} ions from the real wastewater after 6 to 12 days of incubation.

Regarding the removal of Cd^{2+} ions by algae: Feng & Aldrich[18] cite that *Ecklonia maxima* (marine algae) can remove 83.5 mg/g dry algae while research by Kipigroch *et al*. [19] show that using green algae it was possible to remove the concentration of 4.1 mg/L of Cd^{2+} with a yield of 40 to 70%.

Aquatic macrophytes, in general, are recommended in wastewater treatment for the removal of heavy metals by acting as biological filters and by enriching their cellular structure with metal removed from contaminated water. The research carried out by Saraswat & Rai [20] was carried out using the species *Eichhornia crassipes* in the removal of Zn^{2+}, Cr^{3+} and Cd^{2+} ions.

The research reported by Satya Narain *et al.* [21] show that phytoaccumulation is a very useful alternative technique for remediation of heavy metals, because using a free-floating plant (*Water hyacinth*). They investigated the removal of heavy metals such as chromium and cadmium. It was observed that the plants were able to remove Cr^{3+} and Cd^{2+} ions from the municipal contaminated water, respectively, with the average rates 0.10 µg/day and 0.12 µg/day.

Studies developed by Suñe*et al.* [22] show the possibility of removing Cr^{3+} and Cd^{2+} ions from wastewater using the plants *Salvinia herzogii* and *Pistia stratiotes*

Finally, the use of this technique in wastewater treatment depends on the following parameters: specificity of the aquatic plant, microorganisms or yeasts in relation to cadmium ions; concentration of cadmium ions, chemical interferences present in the water, removal speed, costs, among others.

2.1.6. Cadmium recovery from industrial effluents

Due to the increase in industrial activities and the world population, wastewater treatment has become extremely important. Efforts have been dedicated to improving techniques for the preservation and control of pollution with a view to the purification and reuse of water for various uses. Industrial effluents containing cadmium ions have become a serious problem for the environment, considering their strong toxic potential, bioaccumulative and with a half-life of around 10 to 30 years in the human body.

Electrochemical processes are widely used for the removal of metals such as cadmium, the object of this study. The electrochemical cell is the basis of the process, consisting essentially of an anode and a cathode, immersed in an electrolytic solution, as shown in the simplified scheme presented below in Fig. 7.

When the current is applied to the cell, the Cd^{2+} ions are deposited on the cathode, causing the electrochemical removal of the effluent. Electrochemical recovery of metals basically involves two steps: electrodeposition of the metal, followed by some form of re-extraction to remove them from the cathode. The re-extraction process can be carried out by chemical or electrochemical dissolution, by extractive electrolysis or reversal of the polarity of the electrode [23-29].

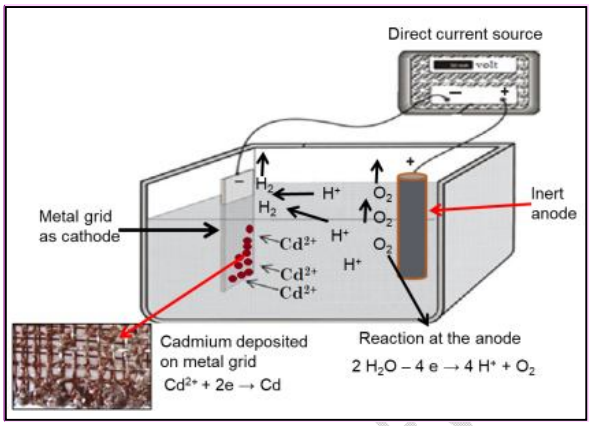

Fig. 7. Schematic of the cadmium deposition cell

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The anodes used in the electrochemical cell are graphite, high-silicon chromium cast iron anode, and platinized anodes, while cathodes can be aluminum, stainless steel, and carbon steel.

The reactions involved in the deposition of cadmium from cadmium sulfate solutions are: $CdSO_4 \rightarrow Cd^{2+} + SO_4^{2-}$

Cathodic reactions: $Cd^{2+} + 2\,e^- \rightarrow Cd$; $2\,H^+ + 2\,e^- \rightarrow H_2$

Anodic reaction: $2\,H_2O - 4\,e^- \rightarrow 4\,H^+ + O_2$

Studies conducted by Dutra *et al*. [25] used a flux Reticulated Vitreous Carbon (RVC) cathode for the treatment of aqueous solutions containing Cd^{2+} ions at the usual concentration found in industrial effluents (15 to 100 ppm). It was possible to treat 2 liters of solution with an initial concentration of 210 mg/L Cd^{+2} to a final concentration of 0.1 mg/L Cd^{+2}, using a deaerated electrolyte (for this purpose N_2 bubbling was performed) at a linear flow velocity of 0.12 m/s in a time of 85 minutes.

Elsherief [26] describes the removal of cadmium from synthetic liquid waste by electroplating cadmium on conventional three-electrode cell using a rotating glassy carbon and Spiral Wound Steel (SWS) electrodes. In this work, a 30% cadmium removal from a 250 mL acid dilute solution is achieved using a current density of 250 µA/cm^2.

Changing the current density to 400 µA/cm^2 yielded a 99.95% removal, for an initial concentration of 500 ppm of cadmium and an operating time of 90 minutes. In the experiment, Elsherief [26] used a magnetic stirrer, using an anode of 25 cm^2 area and the cathode of 550 cm^2 of apparent area and a solution with a volume of 250 mL. It was found that reactions occur in the cathode competing with cadmium deposition, such as the evolution of hydrogen (H_2).

A paper published by Grau & Bisang [27] presents the performance of a bipolar electrochemical reactor consisting of one or more rotating cylinder electrodes of woven wire meshes is that used copper and cadmium deposition from dilute solutions as test reactions. The conditions used in the experiment are: pH=7, T=30 °C, t=10 minutes and initial cadmium concentration less than 650 mg/L.

This article mentions the evolution of hydrogen (H_2), which competes with the deposition of cadmium in the cathode, thus making it difficult to stipulate a relationship between the characteristic parameters of the process. The issue of the current used is also discussed, showing that at low currents there is little cadmium deposition on the cathode and that if there is an increase in the current, the evolution of hydrogen is also increased. It is then suggested that the best current value to use is 2 Amperes. For these conditions, cadmium removal achieved was 38.91%.

To conclude, Butter *et al*. [30] developed a laboratory-scale, multi-step process for the removal and recovery of Cd^{2+} ions from dilute aqueous solutions. Metal removal is achieved by biosorption of the metal cations into a dead *Streptomyces* biomass-free cell suspension in a stirred tank reactor. The eluent is extracted through the biomass filter cake under a soft vacuum, resulting in intimate contact between the eluent and the solids.

Finally, Cd^{2+} ions are recovered from eluate by electrolysis using a rotating cathode cell, resulting in cadmium powder and cadmium-depleted electrolyte that is recycled as eluent. This process is therefore able to achieve very effective Cd^{2+} ions removal and produces only clean water and solid metal, both of which are commercially useful products.

3. CADMIUM AND ITS INDUSTRIAL APPLICATIONS

According to the International Cadmium Association (ICdA) [31] the low cadmium content that occurs in its specific ore (greenockite - CdS) does not justify its commercial mining. However, as it is a by-product of zinc production, cadmium production is directly dependent on zinc refining, especially when mineral concentrates are used, where the average rates of cadmium and zinc extractions are, respectively, 0.23% and 55%.

This fact is also evident in the unequal disproportion of China's annual production, where cadmium production is 8200 t while zinc production is 7236000 t. To complete the world scenario, as seen earlier, the production of cadmium is also linked to the recovery of scrap metal or metal waste containing cadmium.

The scenery of cadmium production use has changed in recent years. Changes in regulation, environmental and health inspection in China resulted in a 35% drop in Chinese consumption between 2017 and 2019. On the other hand, India balanced this drop in China to have a sharp growth in cadmium consumption, mainly by inaugurating a large metallurgical plant for zinc production in recent years, where cadmium is still a by-product [31-33].

The commercial grades of cadmium metal available on the International Free Market have a minimum purity of 99.95% to 99.96%, however, for special

applications such as semiconductors, the grades can range up to 99.9999% purity and are produced by vacuum distillation. Cadmium metal is produced in a variety of forms, such as plates, ingots, and rods, which are used in alloys, pigments, and in the production of cadmium oxide.

Fig. 8 presents the scenario of the applications of cadmium in various industrial uses (2023-2024), which are carefully analyzed below in relation to possible contamination to man and the environment.

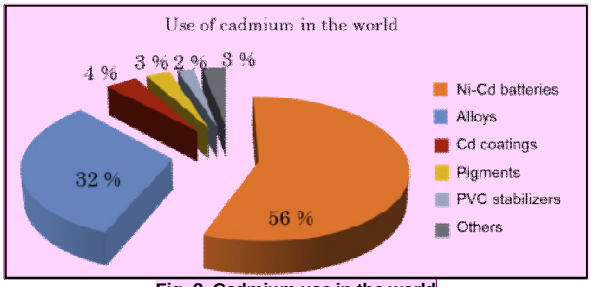

Fig. 8. Cadmium use in the world

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3.1. Ni-Cd Batteries

Ni-Cd batteries have been used in various industrial activities due to their superior reliability and stability when compared to other rechargeable batteries. They are typically used in aviation, public transport, safety and industrial back-up-systems. Additionally small batteries have been used in various electrical and electronic equipment.

The reactions involved in this battery are:

Anodic reaction: $Cd + 2\ H_2O \rightarrow Cd(OH)_2 + 2H^+ + 2\ e^-$

Cathodic reaction: $2\ NiO(OH) + 2\ H_2O + 2\ e^- \rightarrow 2\ Ni(OH)_2 + 2OH^-$

Global reaction: $Cd + 2\ NiO(OH) + 2\ H_2O \rightarrow Cd(OH)_2 + Ni(OH)_2$

One of the advantages of this battery is that it keeps operating regularly even with a high degree of discharge.Fig. 9 below shows examples of medium and small Ni-Cd batteries.

Fig. 9. Medium and small Ni-Cd Batteries

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Ni-Cd batteries power some battery-powered electric vehicles and are also employed in hybrid electric vehicles. Ni-Cd batteries are also used as buffers in transportable, renewable hybrid-power systems developed to generate electricity in distant locations and in underdeveloped regions.

Industrial-sized Ni-Cd batteries can potentially be employed to store energy produced on wind systems or grid solar. Excess energy generated during periods of low electricity demand could be stored in batteries, from which it would later be dispatched during periods of high electricity demand [31,34-37].

Recycling programs for large and medium-sized batteries from trains, airplanes, hybrid power stations, etc., have recovered more than 75% of these batteries for cadmium and nickel recovery [31].

Research developed by Hung *et al*. [38] show that the Thermal Separation Process that uses high melting temperatures, associated with the use of different additives (limestone and fluxes), transforms the different components of Ni-Cd batteries into ingot, slag and flue gas. Gaseous mass containing metals with a low melting point and low boiling point (Cd, Zn, Pb, and Hg) are recovered by condensation, while ingots containing metals such as nickel, iron, and manganese are directed to other recoveries.

The process using the vacuum distillation furnace has been used in the recovery of cadmium in Ni-Cd batteries considering its low melting point in relation to the high melting point of nickel [39].

Other batteries, particularly lithium-ion batteries, have replaced Ni-Cd batteries in many applications; however, they still do not surpass the superior reliability and stability of Ni-Cd batteries in many facilities where safety is vital.

3.2. Metal alloys with cadmium

As shown in Fig. 8, 32% of cadmium is used in the manufacture of metal alloys for various industrial uses. It is important to emphasize that the low melting point of cadmium in these alloys can cause a serious risk, direct or indirect, of contamination to man and the environment.

For example, the results of cadmium volatilization presented in Fig. 10 were determined through experiments carried out with cadmium-coated steel coupons in resistant glass containers, subjected to a temperature of 120ºC to 220ºC for 4 hours. After the coupons were cooled, the vaporized cadmium coating retained in the glass bottle was analyzed. Vaporized cadmium was determined by differential pulse voltammetry.

Chemical analysis shows that the increase in temperature causes the coating to vaporize, thus allowing dangerous contaminations [40, 41].

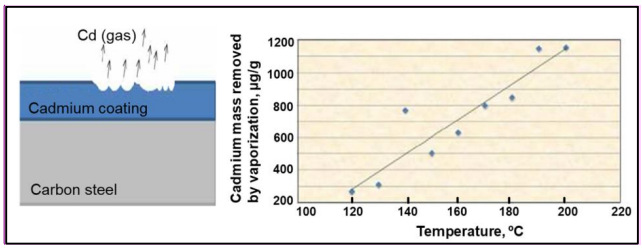

Fig. 10. Cadmium coating vaporization results

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Another point that deserves to be highlighted is the welding operations with cadmium alloys when considering the melting and boiling points of pure cadmium, which are, respectively, 320.9°C and 765°C. This means the possibility of toxic fumes given off containing cadmium contaminating workers and the environment. The referenced literature shows several cases of contamination of welders that occurred during the years they worked with this metal [42-44].

3.2.1. Silver-cadmium alloys

Silver-cadmium alloys are generally made up of 10-15% cadmium and 85-90% silver and are used in many welding applications in heavy-duty electrical installations, especially in relays, switches, and thermostats [45].

3.2.2. Silver-cadmium-indium alloys

This alloy consisting of 80% silver, 15% indium and 5% cadmium is used in the control-rods of nuclear reactors. The cadmium absorbs neutrons, preventing them from creating additional fission events, thus controlling the amount of reactivity [45].

3.2.3.Copper-cadmium alloys

Copper-cadmi*um* alloys are made up of 98-99% copper and 0.1-1.5% cadmium and can sometimes contain small amounts of other metals. They have almost twice the mechanical strength and wear resistance of pure copper while maintaining 90% of their conductivity. These alloys can also be severely cold-rolled and drawn without making them susceptible to softening during heat cycles or soldering.

The basic areas of use of copper-cadmium alloys include auxiliary contact wires, flexible dropper wires and stranded catenary wires for railway overhead electrification, tinsel wires for high flexibility applications, special bunched cables for aviation, military and aerospace uses, and electrical components such as contact strips [45,46].

3.2.4. Lead-cadmium alloys

Lead alloys can contain up to 2% cadmium. The addition of cadmium to the lead alloys gives high strength without affecting the steel wire strength due to the low melting temperature, making it ideal for wire rope socketing. Typical applications include cable cars, cranes, vertical lift bridges and ship hoists. Lead alloys with up to 0.075% cadmium are sometimes used as sheaths for cables subject to cyclic stress [45]

3.2.5. Fuse Alloys Containing Cadmium

Fuse alloys are made up of a solid solution of metals that melt at a certain melting point. According to Jensen [47], Table 4 below presents the year of invention, the inventor, the chemical composition and the melting point of fusible alloys. The alloys containing cadmium are called "Wood", "Lipowitz" and "French", and have a melting point, respectively, at 70 ºC, 74 ºC and 46.9 ºC.

Wood metal" alloy is used in the bonding of metallized ceramic and glass components to metal frames and chassis, where higher soldering temperatures are not possible. Applications include mounting glass lenses during grinding operations, and machining jet engine turbine blades and vanes [45].

Table 4. Types of Fuse Alloys

Year	Discoverer	Composition by % weight	MP,ºC
1701	Newton	50% Bi, 20 % Pb, 30 % Sn	98
1772	Rose	50% Bi, 27.1 % Pb, 22.1 % Sn	95
1775	D'Arcet	49.2 % Bi, 27.6 % Pb, 21.2 % Sn	95
1860	Wood	50% Bi, 25 % Pb, 12.5% Sn, 12.5 % Cd	70
1860	Lipowitz	50% Bi, 27 % Pb, 13% Sn, 10 % Cd	74
Before 1888	Onion	50% Bi, 30 % Pb, 20 % Sn	92
1935	French	41% Bi, 22.1 % Pb, 10.6% Sn, 8.2 % Cd, 18.1%In	46.9

Source: Jensen[47] modified.

3.3. Coatings with electrolytic deposition with cadmium

Currently, about 3% of cadmium production in the world is directed to the electrodeposition of cadmium in various materials and equipment, preferably aiming at anticorrosive coatings in civil and military aviation and offshore activities (parts of electrical equipment, structural parts and fasteners)[48,49].

It is not the objective to compare facts and dates in relation to cadmium, however, historically it is recorded those eighty-four years ago, in the United States, in 1940, during World War II, 75% of American production, at that time, and about 3600 tons of cadmium was destined for cadmium coatings [6].

Cadmium coatings have a number of properties that set it apart as a coating material. These properties include:

- High resistance to salt water corrosion;
- Provides adhesives with an exceptional bonding surface;
- Serves as a great conductor of electricity;
- It is resistant to mold and bacteria;
- Can easily coat different materials, complex shapes, and hard-to-reach contours;
- Can be applied in an ultra-thin, light weight layer;
- It has lubricity that prevents galling and provides a low-friction surface;
- Has a high level of solderability.

The electrodeposition process consists essentially of an electrolytic cell equipped with a direct current source, a cathode (negative pole) where the sample is fixed, a consumable anode (positive pole) of cadmium or an inert anode as shown in Fig. 7. The electrolyte is made up of a solution of Cd^{2+} ion salts and additives that are used to improve electrolyte deposition.

The cathodic and anodic reactions related to cadmium deposition and dissolution of the cadmium consumable anode are presented below [24]:

Cathodic reaction: $Cd^{2+} + 2e^{-} \rightarrow Cd$;

Anodic reaction: $Cd - 2\,e^{-} \rightarrow Cd^{2+}$

In the practice of electrolytic deposition, the thickness of the deposit can be determined by the following equation:

$$\delta = \frac{Dc\ Eelet\eta t}{6000\ \rho}$$

Where:

δ: coating thickness, cm

D_c : cathode current density, A/cm^2

E_{elet}: electrochemical equivalent, g/ A h

η : cathode efficiency, %

ρ : density, g/cm^3

t: exposure time, min

The performance of electrolytic deposition is a function of several parameters that control, directly or indirectly, the final coating applied, such as; electrolyte composition, interfering cathodic and anode reactions, contaminants, part geometry, temperature, agitation, etc.

The composition of the electrolyte is directly related to the substrate, the coating applied and its use. They are usually complex formulations due to the compatibility of the mixture of several substances, such as: salts, complexants, neutralizers, brighteners, acidifiers, surface tension reducers, buffers, dispersants, etc.

Depending on the pH, it is possible to classify electrolytes into acids and alkalines (cyanide-based), whose compositions and operating conditions are presented in Tables 5 and 6 below.

Table 5. Acid electrolytes for electrolyte deposition of cadmium

Comment [A34]: Reference?

Conditions/Composition	Acid Electrolytes			
	Acid 01	Acid 02	Acid 03	Acid 04
Cadmium fluoborate, g/L	240	240	241	-----
Cadmium sulfate, g/L	------	-------	------	50
Boric acid, g/L	22.5	------	27	------
Sulfuric acid, g/L	-----	--------	------	50
Ammonium fluoborate, g/L	60	8	166	------
Temperature, °C	21 – 38	21 – 37	18 – 57	20
pH	3.0 – 3.5	3.0 – 3.5	3.0 – 3.5	--------
Current density, A/dm^2	3 – 6	3 - 6	3 - 6	1.5 - 2
Voltage, V	4 – 6	---	4 - 6	---

Table 6. Cyanide-based alkaline electrolytes for electrolytic cadmium deposition

Comment [A35]: References?

Conditions/ Composition	Alkaline electrolytes (cyanide)			
	Cyanide 01	Cyanide 02	Cyanide 03	Cyanide 04
Cadmium oxide, g/L	30	23-35	17 - 23	22.4 –39.0
Sodium cyanide, g/L	81.2	90 - 120	70 - 90	86 - 131
Sodium hydroxide, g/L	18.7	-----	------	-----
Temperature, °C	21 - 35	20 - 35	20 - 35	20 - 32
Current density, A/dm^2	0.5 - 5	2 - 3	2 – 3	3.2 – 6.4
Voltage, V	6	5 - 6	5 - 6	4 - 6

To ensure the good performance of the cadmium coating, it is necessary to inspect the deposit quality during the electrolytic deposition processing or in the final finished product.

Generally, the control of all stages of the deposition process is done by the manufacturer, although, depending on the volume of production and an agreement between the parties, the customer may participate in the monitoring of the stages to make sure of the quality of the final product.

The follow-up should include the evaluation of the deposition technology, the electrolyte control techniques, the equipment used in the deposit evaluation and, finally, the technique of preparing the surfaces of the samples (parts) to be coated.

After deposition the cadmium coating should be passivated to enhance anticorrosive protection or to form bright layers with other purposes. The passivation processes used are chromatization with chromic acid ($CrO_3.H_2O$), acidic hydrogen peroxide (H_2O_2) and dilute nitric acid (HNO_3). Of those three techniques, chromatization is the more extensively used. The thickness varies from 0.1 mμ to 2.0 μm.

The evaluation of the quality of deposition in the final product must meet the following items: coating thickness, coating uniformity, adherence, porosities and/or failures, hydrogen embrittlement and corrosion resistance [24].

3.3.1. Cadmium layer thickness and uniformity

The thickness of cadmium coating depends on their intended utilization. Minimum thickness criteria for cadmium coating on steel show: severe (12-25 μm), moderate (8 μm) and mild conditions (5 μm). Usually the electrolytic processes furnish uniform deposits, however depending on salts concentrations, on additives used in the bath and on the operational conditions used during the cadmium coating.

These defects are serious mostly when the coated piece is due to be exposed to aggressive conditions. The micrographs exposed in Fig. 11 show, respectively, uniform and non-uniform coatings of cadmium applied on carbon steel.

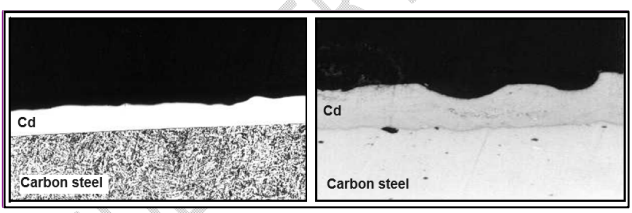

Fig. 11. Uniform and non-uniform cadmium coatings

Comment [A36]: References?

3.3.2. Adherence

Adherence tests are qualitative and comparative and depending on the geometric characteristics of the piece specimens cylindrical or rectangular coated at the same time as the piece are used. They probably acquire the same coating characteristics of the piece itself. The most used test is of the bending or impact types. Usually cadmium coating show good adherence to the base metal.

3.3.3. Porosity and cracking

The cadmium coating should be free of porosities and /or cracks since this kind of defect allows the contact between the corrosive environment and the base metal. The thickness and the uniformity of the coating determine the porosity. When the coating thickness is less than 5 μm a high porosity should be expected, but when it is greater than 10 μm no porosities are found. Fig. 12 shows a faulty cadmium coating.

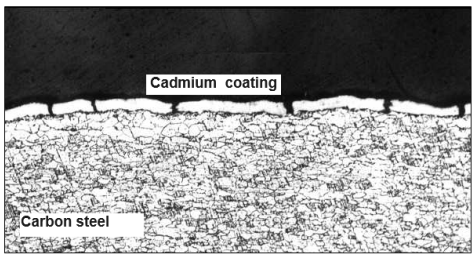

Fig. 12.Cadmium coating cracking

Comment [A37]: References?

3.4. Cadmium-based pigments

According to Turner [50] estimates suggest that annual consumption of cadmium-based pigments peaked at around 6000 tons in 1975, with 90% used in plastics. Due to the strong stance of environmental and public health agencies around the world on cadmium toxicity, annual production has fallen sharply to about 100 tons.

Cadmium pigments(cadmium sulfide and cadmium sulfoselenide) are significant additives in certain specialized plastic, glasses, ceramics and enamels which enable them to achieve bright colors along with long service life, even in very demanding applications. It should also be emphasized that cadmium in these applications is in a chemically stable, highly insoluble form and is embedded in the product matrix.

Research conducted by Turner [50] with various types of contemporary and historical (non-metallic) consumer goods in which cadmium is present in the form of pigments consisting of cadmium sulfides and cadmium sulfoselenides show that small amounts of cadmium appear to be heterogeneously dispersed among consumer plastics, probably an effect that can be attributed to the recycling and the blending of electronic waste and for polyvinyl chloride (PVC).

Turner [50] concludes that, although the typical concentrations reported are within recent regulatory limits and are unlikely to pose a significant risk to consumers, the widespread occurrence of the metal highlights the poor and inefficient practices involved in sorting and managing end-of-life products, and in particular plastic housings of electronic equipment.

Some researchers argue that the encapsulation of these pigments in the polymeric matrix can reduce the level of contamination to humans and the environment, however, such facts do not reduce the level of contamination at the end of the life cycle of the material.

Research developed by Liu *et al.* [51] highlights the oxidation of CdS and CdSe pigments that can occur by photosensitivity, transforming them into soluble products such as cadmium sulfate ($CdSO_4$) and cadmium selenite ($CdSeO_3$).The contact of these compounds with acids promotes dissolution and environmental contamination.

3.5. Polyvinyl Chloride (PVC) Stabilizers

Cadmium laurate ($C_{24}H_{46}CdO_4$) and cadmium stearate ($C_{36}H_{70}CdO_4$) are cadmium organic salts and may contain 5 to 15% cadmium by mass. They are used as effective stabilizers for polymers, especially for polyvinyl chloride (PVC) and its related products, to develop good initial color and clarity, as well as to slow down degradation against heat and ultraviolet (UV) radiation [50].

Because they are heat-stable and resistant to ultraviolet light, cadmium organic salt-based stabilizers are used extensively in outdoor plastics such as window frames, doors, and drainage systems, but they are also used for furniture, office equipment, apparel, clothing and electrical wiring insulation.

Polyvinyl chloride (PVC) is one of the most widely used thermoplastics but is also a material of concern because of the generation and release of harmful chemicals during its life cycle. Amongst the chemicals added to PVC are cadmium organic salt -based stabilizers.

Considering the toxicity of these stabilizers and the association with the recycling of plastics, it is essential that they be prohibited in applications in food packaging, beverage cups and bottles, pharmaceutical product containers, and in the packaging and manufacture of children's toys.

4. HUMAN EXPOSURE TO CADMIUM

In 1910, in Japan, on the borders of the Jintsu River, some farmers protested against the discarding originating from zinc and lead mining, which contaminated the rice paddies along the river. At the time, they were not properly informed as to the seriousness of this industrial dump [52].

The mining company, between 1932 and 1940, tried some preventive measures, however, with the worsening of World War II and the war with Korea, there was a vertiginous increase in the production of lead and zinc, to meet the impositions of the war. However, as the war aggravated, the preventive measures have been largely set aside.

Because their main food was fish and rice from the rice paddies planted on the banks of the river, the peasants and fishermen began to suffer rheumatic pain and myalgia from the industrial effluents of this lead and zinc processing industry where cadmium was an unused by-product.

The disease, caused by cadmium, a natural contaminant of this processing, became known in medical science as "*Itai-itai*". It acquired this name because the victims moaned a lot and "*Itai-itai*" means the groan of pain "ai-ai". It is characterized by sudden pain in the lower back, back, and joints.

Itai-itai's disease, a disease caused exclusively by exposure to cadmium, is defined as a form of renal osteomalacia, a disease that mainly affects postmenopausal women and is characterized by affecting the kidneys and bones, causing fractures and severe pain in the legs and back. The bones become so fragile that they can fracture very easily [52-53].

The disease was only officially recognized from 1968 onwards, with 181 people considered to be clinically infected with the *Itai-itai* disease, while another 330 people were under active control. In 1971 the mining company was found guilty, being forced to pay compensation to the victims caused by the cadmium

contamination, while the local government recovered part of the area and continues to monitor about 1,500 hectares of areas contaminated by cadmium.

The literature reports cases of cadmium accumulation in the human body that may be responsible for or associated, directly or indirectly, with toxic effects on the kidneys, lungs, and reproductive system. In addition, its accumulation in the body can also be responsible for the development of hypertension, heart disease, emphysema, muscle atrophy, and porosity in the bones [54-56].

In the scenario of this decade, cadmium has been seen as an important pollutant for the world, considering the consumption and use of this metal, directly and indirectly, in the various industrial segments, as shown in Fig. 8. Finally, it is valid to affirm that the associations and integrations of industrial practice, mineral use, refining, recycling, industrial effluents, cadmium electrodeposition, municipal burning of solid waste have effectively contributed to dissipate cadmium over the years, contaminating the air, soil, groundwater, plants, animals and man, as shown in the diagram in Fig. 13 [7].

It is important to inform and report the occurrences with contamination bycadmium fumes that occur during welding operations in the industrial electrical system that use silver-cadmium solders that have 15% cadmium.Occupational exposure to cadmium occurs mainly by inhaling fumes from cadmium-containing alloys during the welding process. If there is no equipment to suction these toxic fumes or a personal welder protection system and there is exposure, the first symptoms of poisoning in workers are noticed in a short period of time, causing chills, fevers and headaches [42,43, 57].

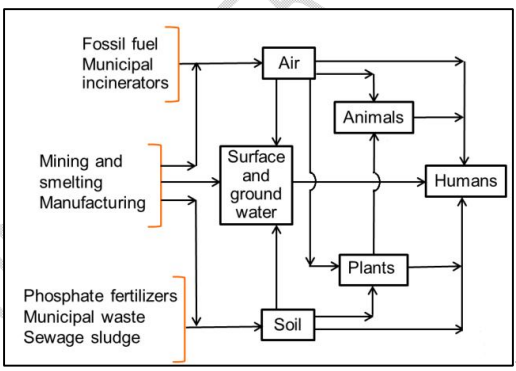

Fig. 13.Schematic representation of cadmium sources to humans.
Source: Liewellyn [7]

5. EXAMPLES OF LABORATORY EXPERIMENTS AIMING TO SHOW THE BEHAVIOR OF CADMIUM IN VARIOUS SEGMENTS

In order to present the knowledge and at the same time awaken the critical view of the behavior of cadmium in the themes presented in this study, simple laboratory experiments were selected and developed, which are described below.

5.1. Experimental validation of the discovery of cadmium by Friedrich Strohmeyer in 1817

This simple experiment aims to demonstrate the surprise of the color changes observed by Friedrich Strohmeyer, in 1817, in the thermal decomposition of cadmium carbonate and zinc carbonate. The yellow coloration indicated a new element that was unknown at that time, namely cadmium [58-60].

The experiment consists of two test tubes in which 1 g of zinc carbonate is placed and 1 g of cadmium carbonate is placed in the other. The tubes are then heated as shown in the diagram revealed in Fig. 14. The yellow residue indicates the formation of cadmium oxide.

The reactions involved in the thermal decomposition of zinc and cadmium carbonates are presented below:

$$ZnCO_3 \rightarrow ZnO\ (white) + CO_2$$

$$CdCO_3 \rightarrow CdO\ (yellow) + CO_2$$

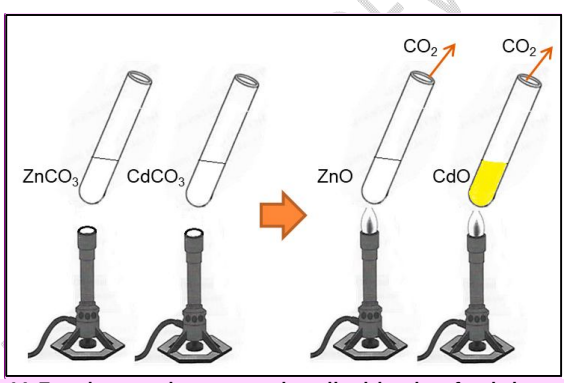

Fig. 14. Experiment to demonstrate the yellowish color of cadmium oxide

Comment [A38]: References?

It is important to emphasize that these experiments should be carried out in a fume hood with good exhaustion of the gases to avoid contamination of the laboratory environment.

5.2. Removal of cadmium ions (Cd^{2+}) in industrial effluents

Wastewater treatment has become extremely important considering the increase in industrial activities. Efforts have been dedicated to improving techniques for

the preservation and control of water pollution with a view to water purification and reuse.

One of the methods used in industry for the removal of heavy metals, as is the specific case of Cd^{2+} ions, is chemical precipitation. This process involves the addition of reagents that causes the metal to precipitate. Hydroxides, carbonates and sulfides are usually used.

The experiment consists of placing 10 mL of 1 M cadmium nitrate in three test tubes and then, respectively, in each tube, 10 mL of solutions 1 M of sodium hydroxide, 1 M of sodium carbonate and 1 M of sodium sulfide, as shown in the diagram in Fig. 15.

The reactions involved in this experiment are:

$$Cd(NO_3)_2 + 2\,NaOH \rightarrow Cd(OH)_2 + 2\,NaNO_3$$

$$Cd(NO_3)_2 + Na_2CO_3 \rightarrow CdCO_3 + 2\,NaNO_3$$

$$Cd(NO_3)_2 + 2\,Na_2S \rightarrow CdS + 2\,NaNO_3$$

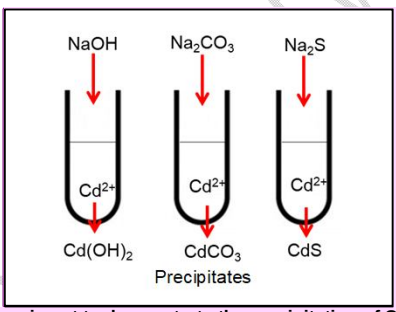

Fig. 15. Experiment to demonstrate the precipitation of Cd^{2+} ions in effluents

Comment [A39]: References?

It is important to emphasize that these experiments should be carried out in a fume hood with good exhaustion of the gases to avoid contamination of the laboratory environment.

5.3. Transformation of cadmium sulfide (CdS) into cadmium sulfate ($CdSO_4$)

In some cases the existence of insoluble cadmium sulfide (CdS) in an electrolyte causes problems during the electrolysis of cadmium metal. To improve the process, it is essential to add hydrogen peroxide (H_2O_2) in order to transform cadmium sulfide into cadmium sulfate, which is soluble, as shown by the following reaction [11]:

$$CdS + 4\,H_2O_2 \rightarrow CdSO_4 + 4\,H_2O$$

The experiment consists of the preparation of cadmium sulfide obtained from the reaction of 5 mL of 1 M cadmium nitrate with 1 M sodium sulfide in a test tube. Wait for the yellow CdS precipitate to deposition at the bottom of the tube and decant the supernatant liquid. Then, add 10 mL of hydrogen peroxide (H_2O_2) and heat until it is transformed into cadmium sulfate as shown in Fig. 16.

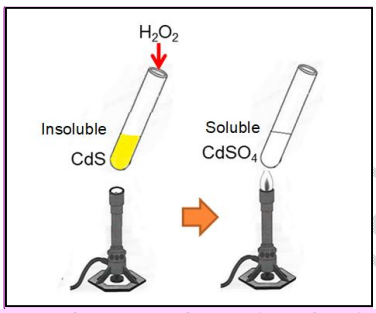

Fig. 16. Experiment to demonstrate the transformation of CdS into $CdSO_4$

Comment [A40]: References?

It is important to emphasize that these experiments should be carried out in a fume hood with good exhaustion of the gases to avoid contamination of the laboratory environment.

5.4. Electrochemical displacement of Cd^{2+} ions present in the solution during the hydrometallurgical process

As seen in Fig. 3, the addition of zinc powder preferentially displaces the Cd^{2+} ions present in the solution based on the electrochemical series presented in Table 7 [61], where zinc has the electrochemical potential of –0.76V and cadmium –0.40 V, according to the reaction:

$$Zn + Cd^{2+} \rightarrow Cd + Zn^{2+}$$

The experiment presented in Fig. 17 consists essentially of a test tube in which 20 mL of 1 M solution of cadmium sulfate are placed. Then, slowly, 500 mg of zinc powder is added. The precipitation of cadmium at the bottom of the tube is noticed, as shown below:

$$Zn + CdSO_4 \rightarrow Cd + ZnSO_4$$

Table 7. Partial List of Standard Electrochemical Potentials

Reaction	Standard Potential Reaction (V vs. NHE*)
$Mg^{2+} + 2\,e^- \leftrightarrow Mg$	-2.37
$Al^{3+} + 3\,e^- \leftrightarrow Al$	-1.70
$Zn^{2+} + 2\,e^- \leftrightarrow Zn$	-0.76
$Fe^{2+} + 2\,e^- \leftrightarrow Fe$	-0.44
$Cd^{2+} + 2\,e^- \leftrightarrow Cd$	-0.40
$Pb^{2+} + 2\,e^- \leftrightarrow Pb$	-0.12

$2\ H^+ + 2\ e^- \leftrightarrow H_2$	0.00
$Cu^{2+} + 2\ e^- \leftrightarrow Cu$	+0.34
$Ag^+ + e^- \leftrightarrow Ag$	+0.80

*Normal Hydrogen electrode (NHE)

Comment [A41]: References?

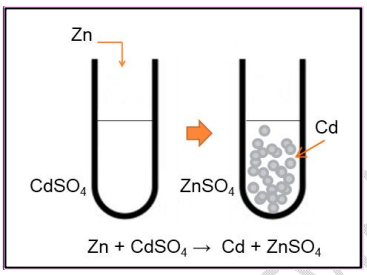

Fig. 17.Cadmium deposition scheme that occurs in the hydrometallurgical process

Comment [A42]: References?

5.5. Evaluation of the reaction of cadmium metal with acids

In these experiments, the main objective is to evaluate the attack of acid solutions on cadmium through the evolution of hydrogen. As shown in Fig.18, two sets are assembled, consisting of a 250 mL Becher, a 50 mL burette and a hydrogen collector funnel, in such a way that the cadmium metal is trapped inside the collector funnel in direct contact with the acid.

As the reaction proceeds, the volume of hydrogen shifts the volume of hydrochloric acid downwards. Solutions of 1M and 3 M hydrochloric acid are used in the comparison. Solutions of sulfuric acid and phosphoric acid can also be used. The reactions are presented below:

$$Cd + 2\ HCl \rightarrow CdCl_2 + H_2$$

$$Cd + H_2SO_4 \rightarrow CdSO_4 + H_2$$

$$3\ Cd + 2\ H_3PO_4 \rightarrow Cd_3(PO_4)_2 + 3/2\ H_2$$

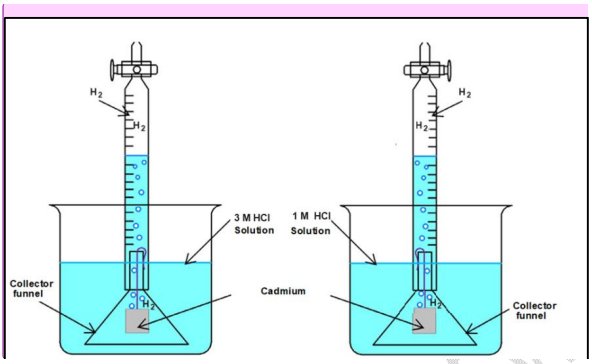

Fig. 18. Laboratory scheme to evaluate the reaction of cadmium with hydrochloric acid

Comment [A43]: References?

5.6. Cadmium electrodeposition process in carbon steel coupons

The scheme of the experiment presented in Fig. 19 uses a 15x15x15 cm acrylic electrolyte cell containing a soluble electrolyte consisting of 12.5 g of $CdSO_4$, 15 mL of 2 M H_2SO_4 and measured in 250 mL with distilled water. The carbon steel disc (cathode) was connected to the negative pole and a cadmium anode was connected to the positive pole.

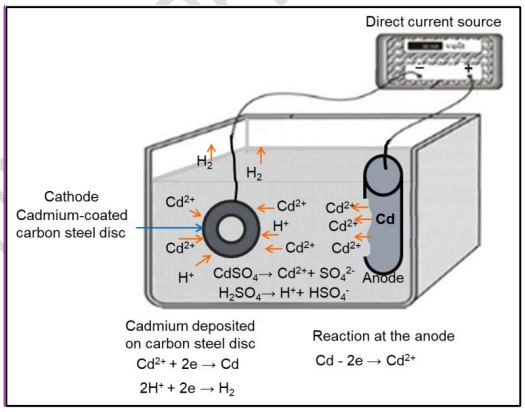

Fig. 19. Cadmium deposition scheme in electrolytic cell

Comment [A44]: References?

The metal surface of the disc was prepared with sandpaper grade 100 until grade 500 and finally, the surface was cleaned with acetone, ethanol and dried with hot

air. The electrodepositions of the disks based on the cadmium electrolyte were: voltage 4.5 V; current density 1.5 -2.0 A/dm^2 and ambient temperature.

Fig. 20 below shows some carbon steel discs that were coated with cadmium in thicknesses of 15 mμ, 25 mμ and 40 mμ.

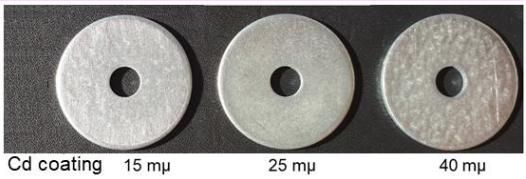

Fig. 20. Aspects of cadmium electrodeposited discs

Comment [A45]: References?

5.7. Chromatization process of cadmium samples

In order to provide a superficial passivation in cadmium samples, as shown in the chromatization mechanism presented in Fig.21, an experiment was proposed to submit cadmium samples in sodium dichromate solution - $Na_2Cr_2O_7$ [62,63].

The experiment consists of placing cadmium pieces in a solution containing 250 g/L sodium dichromate ($Na_2Cr_2O_7$) and 5 mL of concentrated sulfuric acid for 15 to 60 seconds, at a temperature of 25°C. After immersion, the samples are washed under running water and dried with hot air. The final appearance of the pieces is shown below in Fig.22.

Mechanism:

$Cd - 2e \rightarrow Cd^{2+}$

$2\ H^+ - 2e \rightarrow 2H \rightarrow H_2$

$HCr_2O_7^- + 3H_2 + 2\ H^+ \rightarrow 2\ Cr(OH)_3 + OH^-$

$Cr_2O_7^{-2} + 3H_2 + 2\ H^+ \rightarrow 2\ Cr(OH)_3 + H_2O$

$CrO_4^{-2} + 2Cr(OH)_3 + 2H^+ \rightarrow Cr(OH)_3.Cr(OH).CrO_4 + 2\ H_2O$

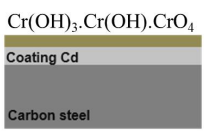

Fig. 21. Chromatization mechanism of cadmium parts

Comment [A46]: Refernces?

Fig. 22. Appearance of cadmium and chromatized samples

Comment [A47]: References?

5.8. Cadmium (Cd^{2+}) ion contamination in salt water from rechargeable Ni-Cd batteries

The experiment aims to show the deterioration of Ni-Cd batteries in salt water and the probable contamination of cadmium in the form of its ions (Cd^{2+}).

The test consisted of placing Ni-Cd batteries in acrylic containers measuring 10x10x8 cm. The corrosive medium used to represent seawater was a solution of sodium chloride (3.5 wt. %) containing 800 mg and 400 mg, respectively, of magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$). The pH was set between 7.2 and 8.0 by addition of sodium hydroxide (NaOH).

To increase the reactivity of the batteries, the plastic wraps were removed and finally the batteries were dented to speed up the corrosive process.

Fig. 23 shows the images of the immersion of the Ni-Cd battery where after 3 days the corrosion of the carbon steel casing begins up to 60 days of immersion in sodium chloride solution.

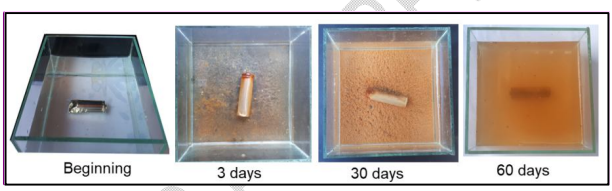

Fig.23.Aspects of immersion of the Ni-Cd battery in sodium chloride solution

Comment [A48]: Refernces?

5.9. Experiments with cadmium welding

According to Choi *et al.* [57] for non-carcinogenic effects, the kidney is the main target organ of cadmium toxicity. Cadmium nephrotoxicity has been well established as; cadmium can induce oxidative stress even at a low level of exposure. While, in chronic exposure to cadmium can induce renal tubular injury, especially in the proximal tubule, including cell detachment, as well as autophagy and apoptotic cell death.

Cadmium is one of the most common carcinogens to which workers may be exposed occupationally, as is the case with contaminations with cadmium fumes that occur during welding operations in the industrial electrical system that use silver-cadmium solders that have 15% cadmium [57, 64,65]

If there is no equipment to suction these toxic fumes or a personal welder protection system and there is exposure, the first symptoms of poisoning in workers are noticed in a short period of time, causing chills, fevers and headaches.

In order to evaluate the contamination that cadmium-containing welds can contaminate a worker, a simple experiment is proposed, consisting essentially of an exhaust fume hood to capture the fumes exhaled by the welding operation, as shown in Fig. 24. A U-tube containing cotton, previously weighed, can

quantitatively determine the content of metals present in the fumes in a given time. In addition, absorbers with hydrochloric acid and sodium hydroxide can absorb the gases that have passed through the U-tube.

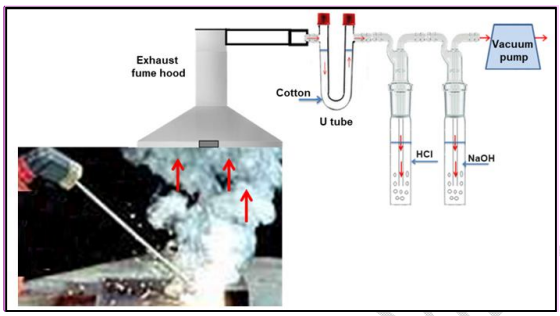

Fig.24. Diagram for evaluating fumes from welds containing cadmium

Comment [A49]: References?

6.CONCLUSION

Based on the study carried out, 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 understanding the industrial routes that use cadmium and the possible aggregations of contaminants during industrial processing;
- It is important that the origin, process and specific properties of the cadmium produced are known in order to ensure the quality of its use in the various industrial segments;
- To ensure the performance of cadmium coatings, the deposition process must be known (acidic electrolytes or cyanide-based electrolytes), as well, the establishment of criteria, procedures and inspection standards during processing and in the evaluation of the final finished product;
- Cadmium coatings should not be used in equipment of food, pharmaceutical and related industries considering their toxic effects on human beings;
- It is essential to monitor and treat effluents from industries that use cadmium in order to ensure the integrity of the environment;
- The systems for the reuse and recycling of materials that use cadmium must be inspected and monitored in order to ensure the integrity of equipment, industrial safety and the preservation of human beings and the environment;
- Occupational exposure to cadmium can be responsible for problems such as: hypertension, liver and stomach diseases, emphysema, cataract formation, muscle atrophy, porosity in the bones, heart disease, cancer, memory alteration and cognitive alterations;
- It is important to inform and report the occurrences with contamination with cadmium fumes that occur during welding operations in the industrial

electrical system that use silver-cadmium solders with 15% cadmium. The international literature reports cases of welders who, in a short period of time, presented associated diseases that caused chills, fevers and headaches;

- The laboratory experiments proposed in this study aim to clarify the fundamentals related to cadmium and its compounds;
- Finally, it is important to reinforce the need to clarify to society the toxic and deleterious trail generated by cadmium and its compounds in human beings, health and the environment.

Comment [A50]: Is it conclusion or recommendation please????

Some tips to be considered in writing conclusion:

- Restate your research topic.
- Restate your thesis: remind readers of your main point.
- Summarize the main points and significance or results and reiterate your supporting points: remind readers of your evidence or arguments.
- Write a clincher: with the last sentence, leave your reader with something to think about

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

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