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Chapter 10

Patents related to reducing toxicity caused by heavy metals

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Patentes vinculadas con la disminución de la toxicidad causada por metales pesados

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Patents related to reducing toxicity caused by heavy metals

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1. Background

In Mexico, various industries produce hundreds of thousands of tons of solid waste, some considered to be dangerous, which when deposited in open air, contaminate flora, fauna, groundwater, and sometimes affect humans. Such is the case of tailings (jales) mining (Nahuatl language derived from xalli, meaning sand), where storage is achieved in tailings dams. These activities were carried out since 1887 following the introduction of metal leaching using sodium cyanide. Since then it has been a technique applied throughout the world for the production of gold, silver and other metals. Approximately 300,000 tons of solid waste is generated daily in Mexico from this mining activity.

On the other hand, corrosion on metal structures causes degradation and possibly heavy metal pollution in soils and waters, thereby providing the necessity to protect metallic surfaces from corrosive agents.

The challenge that faces our working group is conducting research related to different public and private institutions in environmental matters, to provide technological packages or prototypes to help mitigate or control environmental pollution. Since this is a task of scientific-technological development that the country requires, the development of investigations carried out in the National Institute for Nuclear Research (ININ) is developed in two large areas: 1) the processing of industrial solid waste, and 2) corrosion and the environment.

2. Treatment of industrial solid waste

2.1 Foundry sands

One of the main problems of industrial solid waste (ISW) is its massive daily production without any treatment to reduce or mitigate its toxicity. These materials include casting sands from the automotive industry, for which ISW were studied to eliminate or mitigate the heavy metal content present in the chemical array of these residues, as detailed below.

2.2. Toxicity alleviation study

There were seven samples from different stages of the production process of an automotive company. Sample 1 is the extraction of grey iron dust. Sample 2 of the rotaclone, refers to area of anti-corrosion air extraction from sewage sludge. The sample number 3 corresponds to green sand recycling system from sand and dust. Sample 4 is from mud in the anti-corrosion area. Samples 5 and 6 relate to pulp from metallic material of cylinder head machines. Finally, sample 7 corresponded to heart disposal sands.

Samples 2, 4, 5 and 6 were treated according to the ecological NTE-CRT-001/88 standards for non-volatile constituents, obtaining the values shown in table 1.

Table 1. Quantitative analysis of foundry sand samples of an automobile industry

	M2	M4	M5	M6
Determination of pH in the stratum	6.40	6.45	7.24	7.10
Dry sludge, wt%	71.81	78.00	9.71	95.58

Samples M1, M3, M7 were not subjected to this treatment because it was dust or sand without aqueous phase.

Once preliminary tests were carried out, qualitative and quantitative analysis for all samples were done using the following techniques.

Qualitative analysis: used neutron activation and identified all the metals present in mud with the exception of lead since this element does not emit gamma radiation.

Quantitative analysis: used plasma emission spectrometry on the sample to obtain elements of mostly commercial interest.

Table 2 shows the results of qualitative analyses carried out by neutron activation, where the total chemical elements of each type of foundry sand are listed.

Table 2. Qualitative analysis of foundry sand of an automobile industry

Sample	Elements	Total
M1	Co, Se, Na, Mn, Mg, Al, Cl, V, Eu, W, Sm, Ce, Sn, Cr, La, As, Sb, Fe, Zn, Br, Cu, K, Ga, y Ba (Pb*)	25
M2 (solid and extract)	Sm, Eu, Cl, La, K, Na, Al, Ca, Mn, Br, Ce, Zn, Co, As, Pb*	15
M3	Co, Se, Na, Mg, Al, V, Sm, Ba, Ce, Sn, Cr, La, As, Sb, Fe, Zn, Ca, Dy, Ti, Ag y Pb*	22
M4 (solid and extract)	Sm, Eu, Cl, K, Cr, La, As, Ga, Sc, Na, Al, Ca, Mn, Fe, Br, La, Sb, Zn, Sm, y Pb*	20
M5 (solid and extract)	Eu, Sm, W, Fe, Cr, K, As, Sb, Ga, Mn, Co, Cu, Na, Al, Cl, Ce, Zn, Au, Ge, Pt, y Pb*	21
M6 (solid and extract)	Sm, W, Fe, Cr, As, Sb, Ga, Co, La, Na, Al, Ca, Mn, Cl, Br, Fe, Coa, Zn, Au, Ge, Pt, y Pb*	22
M7	Co, Se, Na, Mn, Mg, Al, Cl, V, Eu, Sm, Ba, Ce, Cr, La, As, Sb, Fe, Zn Cu, Ti, Ag, y Pb*	21

* Its presence is determined using the technique of plasma emission spectrometry.

Table 3 shows the quantitative results for sample 5 which resulted to be one of the most interesting samples, due to the presence of valuable or toxic metals contained in the chemical component of industrial waste.

Table 3. Quantitative analysis of sample 5								
Sample	Elemental concentration (ppm)							
M5	Cr	V	Au	As	Ge	Co	Pt	Pb
	758	73	29	< 5	26	60	20	72

An analysis using X-ray diffraction was done in order to study the form of existing metallic bonds in foundry sands. Crystallization states as well as existing metal alloys or bonds were identified, such as: $NaAlSi_3O_8$ (albite), Ca_2 ($AlMg_2Si_4O(OH)_2$) (montmorillonite), SiO_2 (cristobalite) $(NaCa)_2$, 2(FeMn), $3Fe_2$, $(SiAl)_8$ (riebequita), Fe_5SiB_2 (iron and silicon diboride), FeSiC (iron and silicon carbide), Fe_2SiTi (titanate iron and silicon), NI-Cr - Fe, Au_4Mn, PbPt, CO_2GeMn, Al_3OH (bayerite), etc. These metallic alloys are included in the chemical component of industrial waste, which is structured with silicon dioxide.

2.3 Treatment of sand casting in coupled thermostatic columns

Thermostatic columns were designed, built and operated for the first time at the National Institute of Nuclear Research. Both the team and the process were patented by ININ in the United States and Mexico [1-3]. The main objective of this system is to eliminate toxicity caused by heavy metals hidden in ISW.

The idea of using ISW in countries such as Germany and Japan originated from activities involved in the exploitation of gases emitted into the atmosphere due to thermoelectric processes. These gases contain sulfur dioxide, which when in contact with rainwater reacts to form sulfuric acid, one of the constituents of the so-called rain acid, mainly responsible for forest deterioration. In these countries, gases were bombarded with electrons in the presence of ammonia, obtaining ammonium sulfate, a product used in agro-industry as a fertilizer. The process generates value-added compost and at the same time, reduces the presence of a harmful environmental gas. The above example provides a message to our working group: pollution can be attacked using options which, once well studied and addressed, could offer positive and sustainable results.

(a) A description of the thermostatic column

The apparatus comprises a Pyrex glass column, which has a heating enclosure or jacket where fluid from a thermostatic system circulates, thereby maintaining a constant temperature (around 60 °C) inside the column according to the variables of the metal extraction process (also known as leachate) from ISW.

This system also includes an air supply source prior to the column, which consists of an air valve, a decarbonator device and a humidifier, these last two on the path connecting the source to the column. Through the decarbonator and the humidifier, air is injected to ensure that it reaches the column through a dispersion system that serves to promote suspension and adequate homogenization of the pulp[1]. The device consists of a membrane with multiple holes of sufficient diameter that does not allow the pulp to cross the direction of air flow.

In order to control air flow supplied to the column, a device has been installed for measuring flow at a point prior to entry into that column. Temperature control of the heating fluid is maintained with devices for thermal control and flow.

(b) Process of metal elimination

The sands are finely milled and suspended in a watery medium, with a ratio of solid to liquid of one to ten and the required reagents were added, i.e. 10 to 40 g of mineral acid or a base with a pH range of 2, 5, 7 and 10. Four to fifteen grams of a bisulfate compounds and 0.3 to 1.5 g of surfactant cationic or anionic were added. The addition of the latter is due to metal ions either being absorbed in foam or co-precipitated in solution. The pulp is processed within the column for 2 hours, with an airflow supply of 1.8 liters per minute per liter of pulp and pH controlled with additions of sulfuric acid or sodium hydroxide. The pH was measured every 10 minutes in the first hour of the process and then every 30 minutes in the next hour in order to achieve this. At the end of the operation, pulp is extracted from the column that recorded consumption of reagents in the following order: 100 g of sulfuric acid, 33 g of sodium hydroxide, and 2 g of dodecyl sulfate sodium per each kilogram of foundry sand. The pulp is then heated to 60 ºC for 20 minutes and passed through a Büchner filter with fine pore filter paper obtaining a solution rich in metallic ions such as gold, silver, platinum, zinc, copper, iron, manganese etc. These metals are likely to be separated using various technologies, where the most recommended is the selective separation of metals using electrodialysis, where the separation is also highly efficient by this method. The recovered metals may be obtained in solutions with a specific metal content, or in powder, to be reused across other applications in the mechanical metal industry: galvanizers, chromates, etc. Although the latter has not been conducted in the laboratory, it is mentioned in the subsection on perspective, because it is offering a comprehensive process where metals in solution will be reinstated to the industry for reuse.

On the other hand, a solid material free of heavy metals was also obtained, which can be used to produce bricks, lattices or ceramic, to be used in the construction industry. This is detailed below.

The pH which allowed better processes for metal leaching from industrial solid waste was in the acid range (pH = 2), while good leaching efficiencies could be obtained at basic pH only on rare occasions. On the other hand, to obtain the largest amount of metal hidden in chemical arrays, it is advisable to perform the largest number of operations on the same sample at optimum pH, as one of the objectives of this study was to investigate the pH range where greater metal extraction efficiency is obtained using thermostatic columns.

[1] It is called the pulp mixture granular solid industrial waste, chemicals and water.

Qualitative and quantitative analysis of extraction liquors were performed by three methods, namely: neutron activation analysis, plasma emission spectrometry and atomic absorption. Each sample was analyzed five times in the case of the last two techniques above, in order to obtain reliable statistical results. After each operation, the column was washed with hydrogen peroxide and then with a mixture of nitric acid and perchloric acid to dissolve materials that had still remained attached to the walls of the column or dispersal device.

The technique through thermostatic columns, allows up to 100% metal recovery such as vanadium, arsenic, chromium, nickel, cobalt, germanium, copper, platinum, gold and silver, as well as 20% aluminum. Two alternatives can be followed for recovering metals from the liquors. One of them is to precipitate all liquor metals together, i.e. a precipitation containing a mixture of metals, and the other is by using a selective method such as electrodialysis technique, as mentioned above.

2.4. Implementation of the metal elimination process from national industrial waste

The industrial park in Mexico consists of a total of 172,599 industrial units (General Directorate of Environmental Regulations, INE SEDESOL, 1992). The volume of waste generation comes from 4 sectors: 1) extractive and mining smelter, which generates 300 thousand tons per day; (2) chemical engineering, basic, organic and inorganic, with 70 thousand tons per day; (3) agro-industry, which generates 29,500 tons per day, and 4) rest of the sector, which generates 15,500 tons of hazardous waste per day. These solid and semi-solid materials contain different concentrations of toxic metals, valuable and susceptible of being recovered, thereby eliminating possible environmental contamination.

In Mexico industrialization began in the 1940s and until 1971 there was no legal restriction to throw ISW or hazardous waste everywhere, and respect for the environment was absent in the perception of the employer. The first ecological standards started to operate at the end of the 1980s, including the standard to determine components that characterize a hazardous waste by its toxicity in the environment. It was under these conditions that in 1990, a company set up in Puebla, Mexico, expressed interest to ININ to characterize and eliminate toxicity, by their content of heavy metals from waste foundry sand.

Foundry sands are used for molding various pieces in the mechanic metal industry, automotive and ceramic, among others. Recalling above-mentioned issue, these sands are contaminated by toxic metals which combine to form alloys when carrying out casting processes, and coalesce, bind and react with the initial product. Our x-ray diffraction studies of foundry sands originating from an automotive industry revealed interesting aspects, such as the presence of manganese-gold, lead-platinum, manganese-cobalt - germanium, chrome-iron alloys - nickel and aluminum-silicon - iron, among others, hidden in silicon dioxide.

Important results were obtained when using thermostatic columns to apply the process described previously. On one hand, the metals extracted simultaneously from the industrial waste can be recycled and, on the other hand, the significant decrease in waste toxicity was used for the production of building materials. The metals which can be recovered by means of this system include: platinum, gold, silver, cobalt, zinc, germanium, manganese and copper, all with a high commercial value. Also recovered were chrome, vanadium and arsenic, which are highly toxic metals.

An agreement with the Federal District Department, through the Committee on Projects and Studies for Environmental Recovery (COPERA) to launch the project "Toxic metals from industrial sludge extraction" was established in 1994. This agreement led several companies in the Valley of Mexico access to provide samples of their industrial solid and semisolid waste. In this way 24 samples were divided into: 4 of chemical companies, 3 foundry companies and 17 in other industrial sectors. Some of the metals that could be extracted simultaneously with a high degree of sample efficiency are: gold, germanium, chromium, arsenic, lead, zinc and iron. These experiences could sanction that the equipment and processes used could be applied to treat different industrial waste with different chemical arrays.

In recent years various aspects of research on this topic has been improved. In 1995 a research paper on the evaluation by PIXE (Particle Induced X-Ray Emission) of the efficiency of an experimental thermostatic column was developed, which was designed to recover metals contained in sands used for motor vehicles casting by leaching. The results of this assessment allowed raising alternative solutions to the problem of storing huge amounts of residual sand contaminated with metals produced by metallurgical industries, because sand, after treatment considered here, could be recycled for other industrial purposes. The work consisted using a beam of 3.55 MeV protons to radiate "open-air" samples from sands of the main casting processes of an automotive plant, as well as to radiate semisolid phase (sludge) samples obtained from the treatment of leached sand in the thermostatic column. Elementary quantitative analysis of samples for PIXE technique allowed determining the degree to which each casting process pollutes the sand, as well as the recovery efficiency for each analyzed element associated with the liquid (liquor), resulting from the leaching process in column [4].

In 1997, samples of industrial wastes from sand casting from an automobile manufacturer established in Cuautitlán, Mexico State, from a painting industry, and from a company of pesticides in Ecatepec, Mexico State, were received [5]. These three samples were processed using equipment and a patented process and once again we could confirm the efficiency of our technology for leaching in industrial solid waste with different composition in its chemical array.

An article on leaching of hazardous industrial waste which includes the diagram of a pilot for the extraction of heavy metals plant, as well as the estimated costs of the same [6] was published in 1998.

Work carried out in 2002 on leaching, using mud and ashes from Reciclagua waste water treatment plant, located in Mexico State Lerma River industrial corridor, coupled thermostatic columns and dietilentriaminpentaacetato acid (DTPA) as complexing agent and demonstrated that the use of the DTAP substantially improved efficiency of leaching extraction processes [7].

In the year 2006, the author appeared as guest editor of the English magazine "International Journal of Environment and Pollution" (IJEP), in which 18 articles of Mexican researchers have been published across three issues of this magazine [9].

2.5 Equipment and design of metal elimination process in solid waste

Equipment have been designed and built for metal leaching processes which are already patented. Figure 1 shows a diagram of the thermostatic column, where its key components can be seen. It is an elaborate double bottom Pyrex glass laboratory column, for the purpose of circulating a fluid (water or oil) in this space to heat the column. The fluid enters the bottom of the column and exits via the superior part. The bottom of the column has a porous glass membrane so that air can enter propelled by a compression and acting on the sludge, which is the mixture of industrial solid waste with different chemical agents. Among the latter is a complexing agent, a reducing agent and a surfactant agent. The process takes 2 hours and the air flow entering the column through the porous glass membrane is 1600 cm^3/min.

Figure 2 shows a diagram of the process used to remove toxic metals from industrial solid waste using coupled thermostatic columns. This process saves energy and time, because each column is used to analyze the leaching process in a specific pH range, and the fluid runs through the four columns. Figure 3 shows a diagram for the installation of a pilot plant, in order to process a ton per hour of different ISW applying columns. The developments in this area have given rise to several bachelor and doctoral degree thesis [10-14].

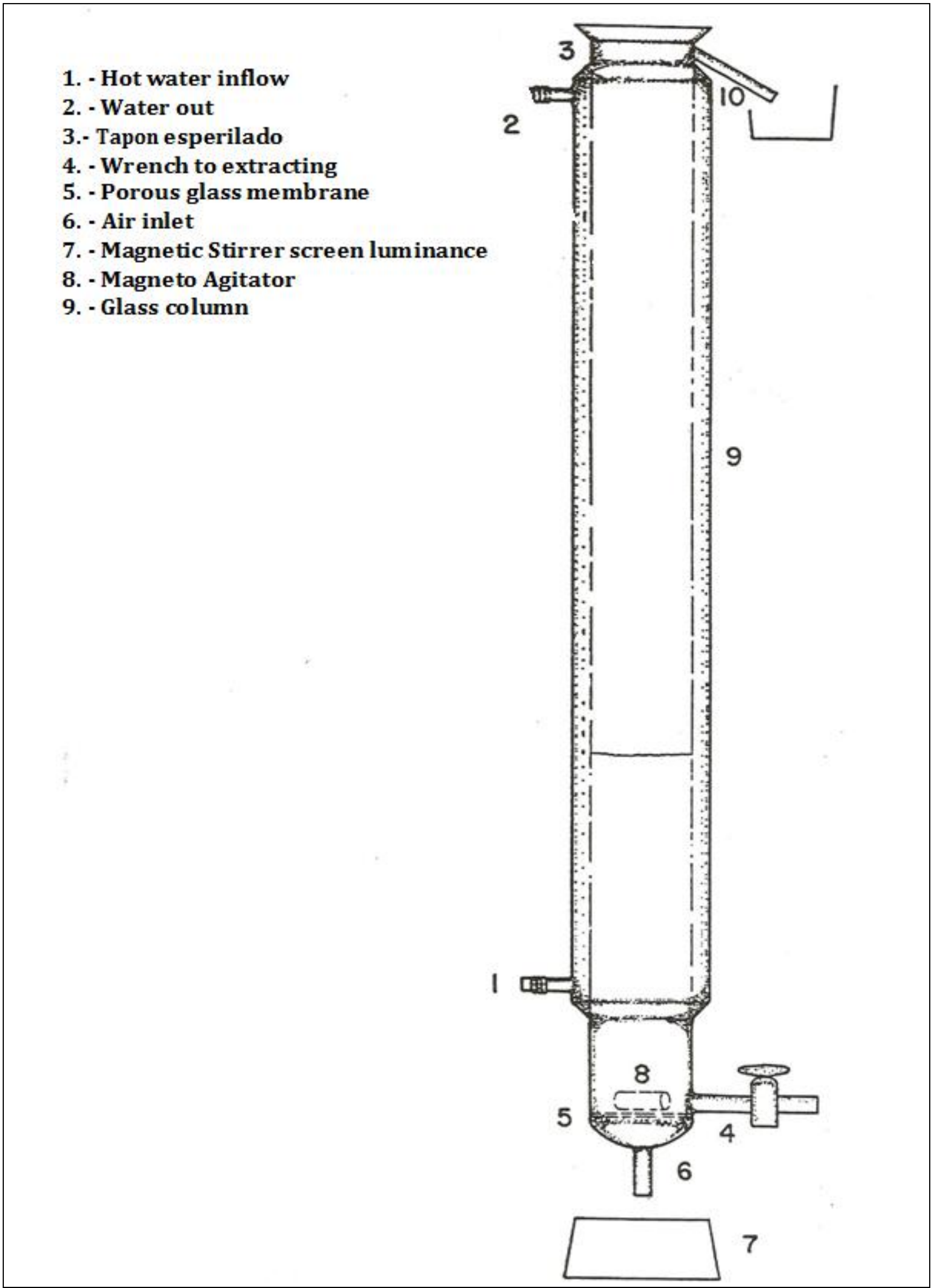

Figure 1. Diagram of thermostated column.

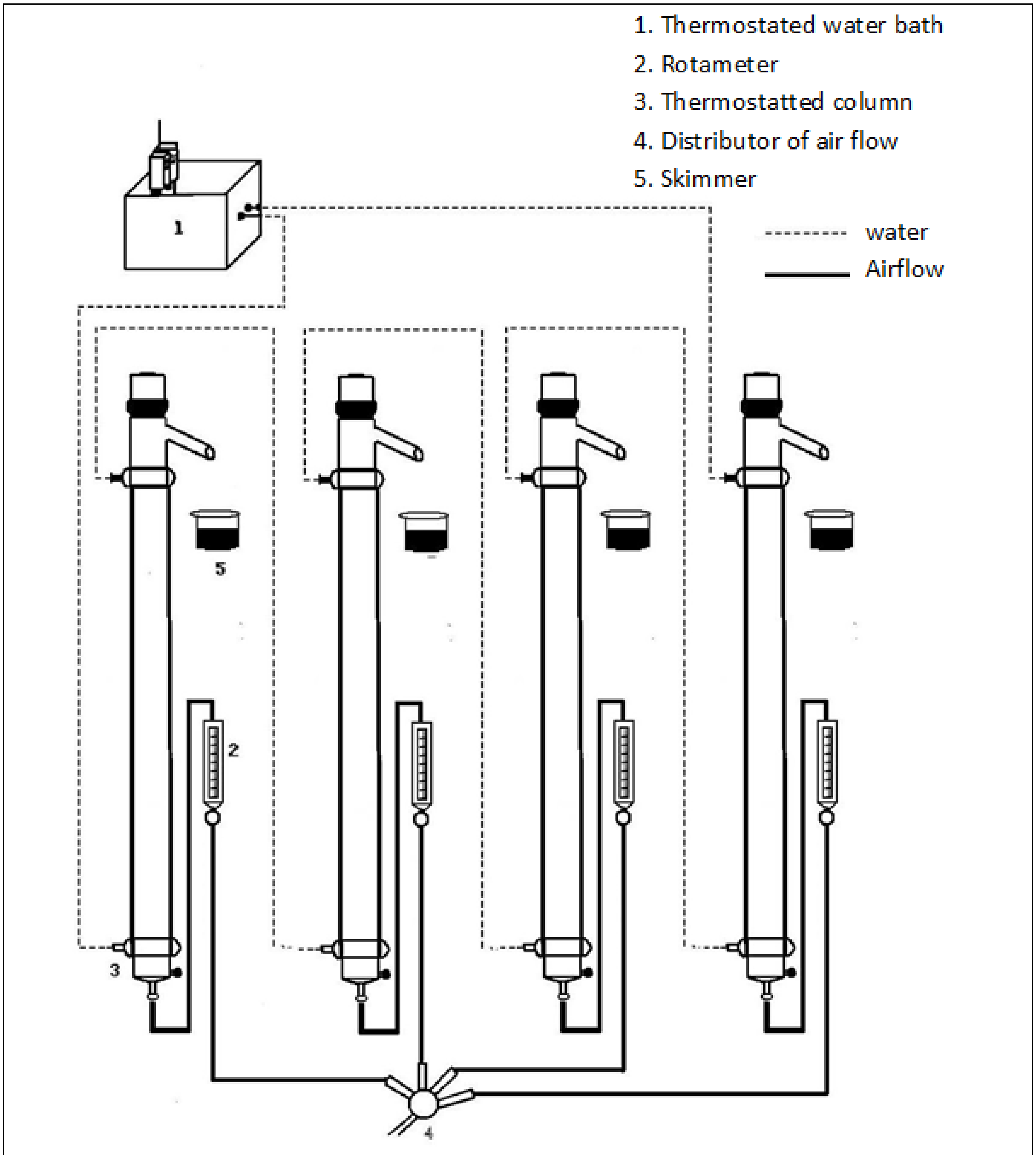

Figure 2. Schematic process of the extraction of heavy metals from industrial solid waste.

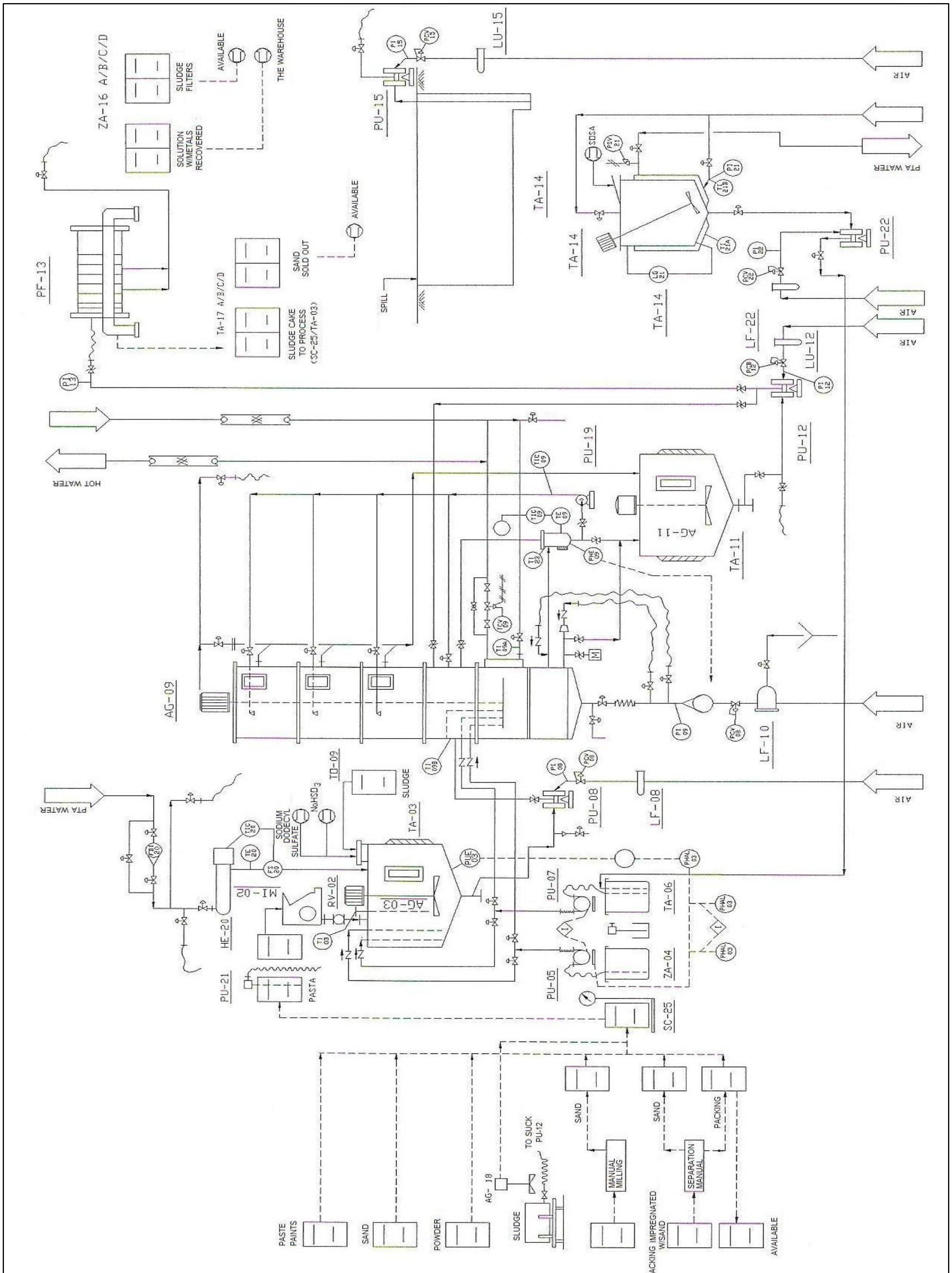

Figure 3. Pilot plant for extraction of toxic metals and precious and semi-solid waste industry, using thermostatted columns.

3. Corrosion and the environment

3.1 Overview on corrosion and strategies to counter it

Our group has also developed work on corrosion on metal structures and its impact on the environment. In this way research has been carried out on bismuth, for which Mexico is one of the major producers [15-16], and phosphated Zn/Mn and chromium phosphate alloys to mitigate corrosion in steel carbon, aluminum and sensitized stainless steel 304. A prototype and a process were developed with the possibility of being applied to nuclear, automotive and mechanic metal industries. This last aspect will be described in the next section.

Corrosion is the destructive attack on a metal or alloy, caused by a chemical or electrochemical reaction under various conditions. Corrosion has been also defined as the process of deterioration of a metal, motivated by interaction with the environment, which affects properties to be preserved. This definition, by extension, is also applicable to non-metallic materials such as glass, concrete, wood, etc., and involves the popular concept of corrosion as a process that requires prevention and control.

The economic aspect of corrosion is one of the main factors that make many researchers to devote their efforts to its study and prevention. Economic losses caused by corrosion add up to millions of pesos. These harmful effects of corrosion are classified as direct and indirect losses.

3.2 Phosphate coating to mitigate corrosion

The need to consider options to prevent the corrosive deterioration of metals, whose products are toxic when they dissolve and are disseminated to the flora, fauna or groundwater, led to the search for a viable alternative, technically and economically, to prevent corrosion.

Phosphate coatings are applied on ferrous and non-ferrous surfaces and are composed of small crystals of zinc, iron, chromium, or magnesium phosphate. These inorganic coatings retard corrosion and promote a greater protective paint adhesion.

Phosphate coatings are used as a primer, i.e. their function is to offer more adherences (also known as "anchor") at the interface between metal and top coating. This can be done with a resin or some anticorrosive paint. The phosphate deposited on the metal is not only stable and chemically inert organic finishes, but also absorb and form a coating to the metal. The most important reason to use a phosphate coating is to prevent or retard the spread of corrosion under the paint, even in the areas close to zones where a rupture may exist.

3.3 Methods of applying phosphate coatings

There are four types of phosphate coatings in use: iron, crystalline zinc, microcrystalline zinc and manganese. Application procedures are briefly described below.

(a) Immersion

All types of phosphate coatings mentioned above can be applied using this method. Application time is approximately 5 minutes and its principal advantage is that it provides a greater coating thickness. This technique is considered to be one of the most widely used and applied for primary phosphate elaborates.

(b) Spray

Iron and zinc phosphate coatings are applied using this method, while manganese does not. This method enables the application time to be less than that of immersion. The spray requires one application no longer than 60 seconds and the thickness obtained on average is 1 to 2 μm.

(c) Phosphate electrochemical

This process takes between 0.5 and 5 minutes from electrochemical polarization, followed by the chemical consolidation deposit for a total time of 14 minutes, thereby achieving a low porosity uniform coating. The disadvantage of this process is the high installation cost and use of an electrical power source.

(d) Coating using a mobile device

Methodology, process, and prototype of the mobile device were developed by our group with the help of various specialists from ININ, conducting operational testing at the Institute. The equipment used to phosphate, mounted on a mobile device, enables an *in situ* process, regardless of the external shape of the substrate. The performance is satisfactory, being possible to phosphate up to 2 m^2 of substrate, with coating thicknesses that vary from 12 μm using aluminum as substrate, to 17 μm using carbon steel with a liter of solution. Another material that has achieved promising results is stainless steel 304, which can be sensitized when a piece is welded and joined to other materials. Sensitization is the process resulting from chromium carbide precipitation at the grain limit, consequently causing the impoverishment of chromium on the metal surface, and becoming more vulnerable to attack from aggressive agents. If the latter occurs, then it is possible to place a phosphate film coating over the welding ridge and nearby areas, later applying layers of paint to protect the metal surface and extend the life of the material.

3.4 Operation of the mobile device

Figure 4 shows the parts and components of the process and equipment to implement the phosphate coating. Phosphate solution heating operations are carried out at an approximate height of one meter above the mobile device (3). The heating is carried out through a thermostatic bath (1) that uses oil, which maintains the solution temperature upon exit at 80 ºC in the case of coating on steel carbon, and 30 °C in the case of phosphate on aluminum. When the desired temperature has been reached, phosphate solution flows by gravity through a flexible thermally isolated non-phosphate material pipeline (2) towards the body of the mobile device (3), which receives the solution and its dispersion and application on the metallic substrate (4) occurs only through the direct contact of the solution and the substrate (4). The remaining solution is collected and sent into a container (5) that may or may not be immersed in an optional thermostatic bath (6). By means of a pump, phosphate solution will be sent back to the thermostatic bath (7) through a non-phosphate isolated heat duct (8).

Figure 5 shows the diagram of the mobile device used for phosphate, consisting of a main body of hemispherical form (11), which is an internal chamber (16) and constructed entirely of nylon. The device has hexagonal nuts (9) to connect to the device (11) with isolated flexible heat duct (2) that carries the phosphate solution. The upper part of the main body (11) of the device has a connector (10) which brings the phosphate solution from the pipeline exit (2) to the body of the device (11). This connector (10) has a lower perforated spherical output (12) to disperse the phosphate solution on the surface to be treated. The interior of the chamber (16) is placed on top of a perforated circular plate (14) where there are a few areas of ceramic material (13) that serve to assist the distribution of the solution into the body of the device, so that it can be spread throughout the circular stripboard (14). Around the perforated circular plate (14), is a circular nut (15) that allows access to the interior of the chamber (16) of the device when cleaning is required.

This process is carried out for the time necessary to obtain the desired coating. The team and the process are patented at the Mexican Institute of Industrial Property [17,18].

The adhesion of film coating, with and without paint, was analyzed according to ASTM D4541-85 and NACE standards. The results showed excellent adherence afforded by film coating in metal-primer and primer-paint interfaces. Corrosion resistance tests were also carried out using the saline chamber, in order to determine metal corrosion and the degree of protection that organic and inorganic coatings provide. Saline chamber is a technique according to ASTM B117, which accelerated corrosion tests on metal probes or samples. The tests applied to steel carbon, aluminum 6061 and aluminum 1300 - T651, showed no corrosive attack, no detachment nor formation of bubbles. On the other hand, the panels that were exclusively painted presented corrosion problems due to rust. Materials that were neither painted nor phosphated showed a severe process of corrosion. Also several bachelor's and master's degree thesis [20,24], on this topic have been published, as well as publications on the use of phosphate coatings in metallic materials in the automotive industry [19].

The latest research carried out in the ININ ensure the possibility to phosphate sensitized stainless steel 304 through the technology patented by ININ applied to steel carbon, which open up perspectives and new applications of this Mexican technology.

4. Perspectives

4.1 Metallurgical

Selective recovery of metals from leaching liquors, applying thermostatic columns of industrial solid waste and using electrodialysis technique, will enable recycling of metals of interest to avoid what is considered a waste, therefore eliminating processing and/or storage costs. Contrarily, the solutions used for sample leaching when processed through thermostatic columns will be recovered. These solutions are recirculated by column to continue the leaching process, promoting comprehensive management of the product in this way and reagents used during the process.

Metal products so obtained have a wide range of possibilities for use, for example:

(a) Obtaining metal powders.

(b) Realization of thin metallic films technology

(c) Metallic deposits by thermal spray or plasma.

(d) Metallic deposits by electrochemical procedures.

Electrodialysis is an expensive technique, which involves the use of anionic and cationic membranes, as well as flow routers, but its implementation will mean the production of pure outputs, which will be selectively recovered.

4.2. In civil engineering

Industrial solid wastes are the result of production processes abandonment, which pollutes the environment. With the proposal to re-use them (via manufacturing of lattices, tiles, blocks, etc.), its volume is reduced, taking advantage of them as raw materials and improving the environment.

The recycling of this waste creates a technology that allows natural resources to be preserved, without affecting the environment with negative impacts on the exploitation of raw materials for the manufacture of building materials. These materials are refractory since, as silicates and the agglomerates (kaolin, clay), have thermal properties that can withstand high temperatures (800 °C) without altering its structure. The choice of agglomerate is based on the characteristics of the solid materials (sand casting, mining waste, diatomaceous earth, etc.), whereas the agglomerate (kaolin, clay) must be inexpensive and possess positive mechanical properties in the manufactured material.

4.3 Agricultural

A treatment plant is located in the industrial zone of Toluca, whose mud and ashes contain large amounts of hidden metals which are likely to be recovered and taken advantage of, thus recommending that the process and equipment are used in the thermostatic column.

The DTPA is an important chelating agent, which forms very stable complexes with a large number of metal ions. Through its use, it was possible to obtain better metal leaching efficiencies from sewage sludge and ash, as compared to the leaching process, which was not used. However, given its high cost, its use could be limited, so it is necessary to continue to more experimental work with other less expensive complexing agents.

This first step towards metal recovery in ash and mud promotes studies to acquire a greater amount of metals from ISW and furthermore, given that the byproduct (solid waste and leachate) saves a large amount of nitrogen and organic material, in this perspective it will be recommended for use as fertilizer.

4.4. Pilot plant for industrial solid waste treatment

As mentioned in this work, the daily production volume of ISW in Mexico and probably globally adds up to several hundred thousand tons, justifying the need to create the compilation waste centers mentioned in different sectors. For example, in the Valley of Mexico, one could be located in Ecatepec, another in Naucalpan, one in Vallejo, etc. Each of these centers could have a facility for waste treatment, receiving value added for decontaminated and solid leaching liquor products on one hand, and encouraging jobs creation on the other hand. Therefore, an additional benefit would prevent this waste to be left under the open sky and at the same time promote the establishment of regulations to ensure that companies treat their wastes. In this aspect, ININ has preliminary parameters for the installation of a pilot plant, as mentioned previously in this work.

4.5 Phosphate coatings in different industrial sectors

The serious problem of metal contamination derived from metal structure deterioration due to corrosive substances, as well as the need to avoid fatal accidents by corroded metal parts, like the one which happened in the city of Guadalajara in the 1980s, makes important to educate industries on the maintenance of their metallic structures, so that they should be followed by developing studies and applications of phosphate coatings using mobile devices in metals such as zinc, sensitized stainless steels, copper, etc. Also, normalize and standardize the preventive and corrective maintenance of the metallic structures of companies. It is worth mentioning that the National Institute for Nuclear Research has developed the prototype of a mobile device for the application of a phosphate coating, useful for both academic dissemination and industrial application.

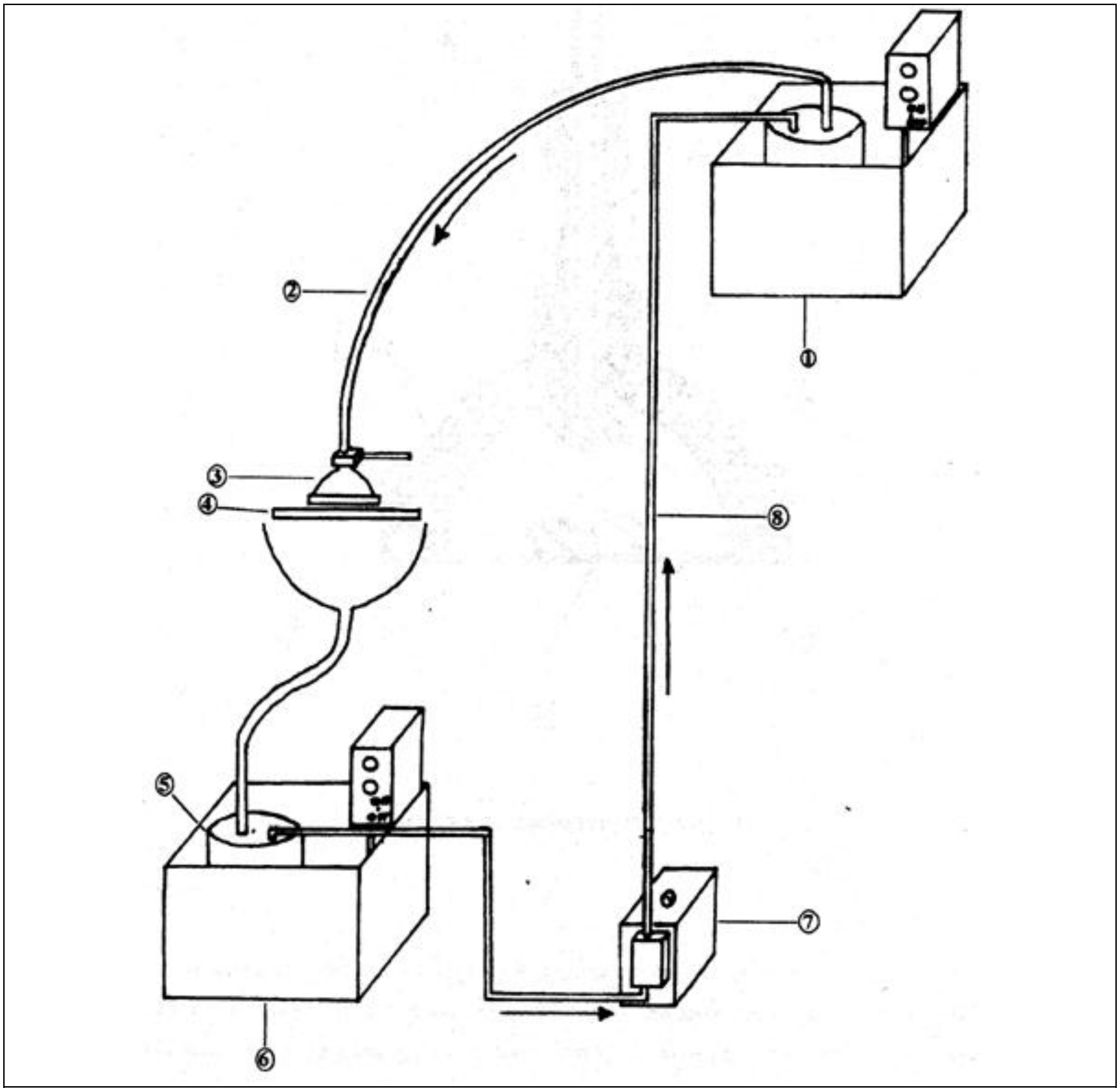

Figure 4. Phosphating process using the mobile device.

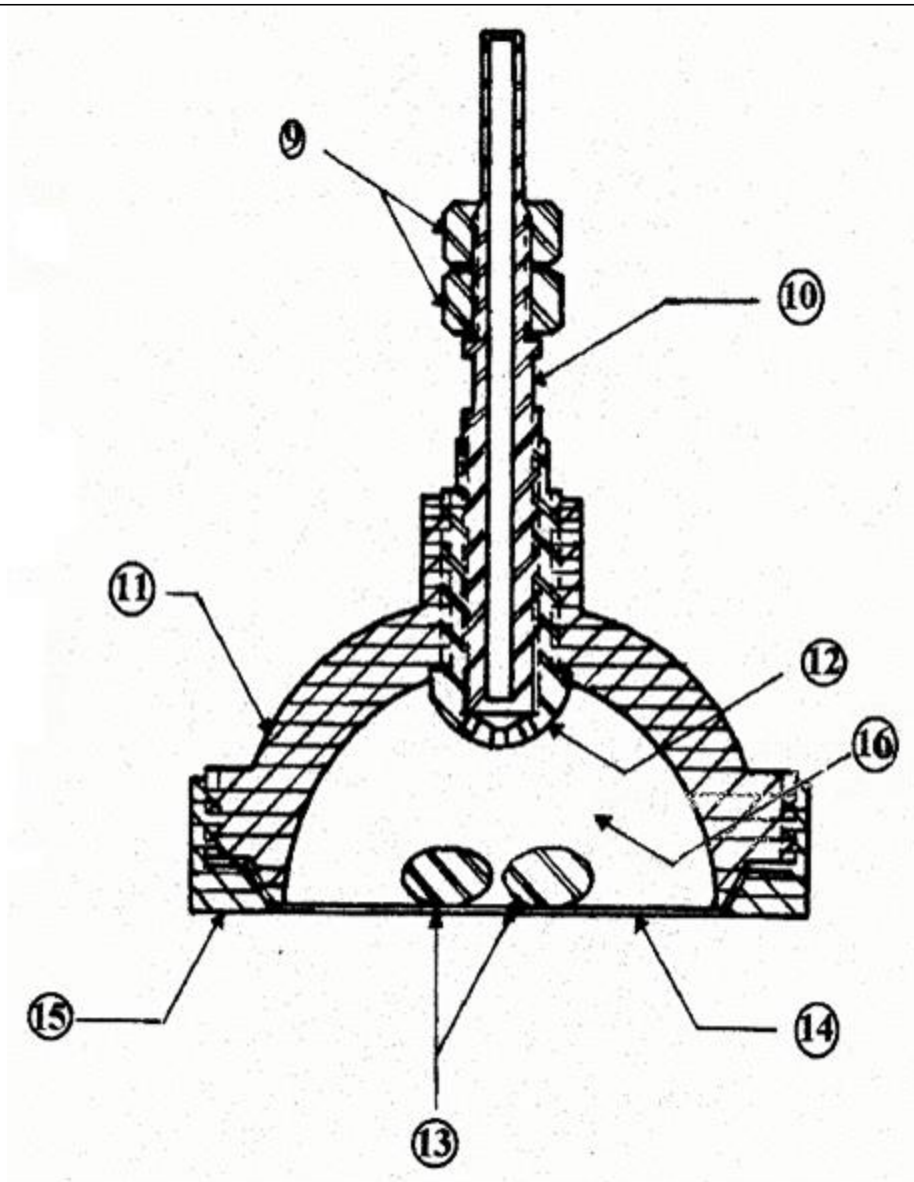

Figure 5. Mobile device for phosphating process.

5. Conclusions

We obtained two patents under concession in the United States of America, one for the leaching process from foundry sand, and the other for the ISW leaching equipment. With this Mexican technology it is possible to recover valuable metals such as gold, platinum, silver, cobalt and titanium, among others, as well as highly toxic metals like arsenic, lead, chromium and vanadium. All these metals are capable of selective recovery using membrane separation technologies, for industrial reuse. Likewise, a patent of the same process and equipment was obtained in Mexico at the Mexican Industrial Property Institute (IMPI). Research done subsequently confirmed that it is possible to retrieve other ISW metals, such as those coming from the mining industry (tailings), diatomaceous earth, electroplating, sludge and ash from incinerators. A technological package has also been developed, containing a preliminary diagram for the installation of a pilot plant to treat the ISW in different industries, to eliminate the accumulation of stored waste pits, whose toxic elements migrate to the flora, fauna and eventually to humans, producing in the latter a variety of diseases and possibly death. It has also the purpose of using solid waste leachate to develop ceramic materials or construction materials, obtaining a value-added processed material, whose excellent physical and mechanical properties are optimal for the construction industry.

Another important contribution of the work carried out by our group has been the patenting at the Mexican Institute of Industrial Property (IMPI) of two processes and its respective equipments: one to phosphate carbon steel using a mobile device, and a second one to phosphate aluminum, also using a mobile device. These materials are essential in the nuclear and automobile industries, aviation, shipping, etc. The Mexican technology extends the useful life of metallic materials and reduces the emission of toxic metals in the environment due to corrosive processes.

Phosphate coatings applied using the thermostatic mobile device, can be used on fixed metal structures or on structures that are difficult to transport. With the process and equipment described in this paper, it is possible to obtain phosphate coating thicknesses of 12 μm in aluminum and 17 μm in carbon steel. It offers excellent adhesion on metal-primer and primer-paint interfaces, as well as high corrosion resistance. Recent research carried out at ININ has confirmed that it is possible to implement the coating patented technique on surfaces of sensitized stainless steels, expanding the uses and prospects of this Mexican technology. The National Institute of Nuclear Research has developed a prototype of this equipment for academic dissemination and implementation.

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