Treatment of Acid Tars by Encapsulation to Reduce the Effects of Pollution on the Environment

MIHAELA TITA[1], DANIEL TITA[1], ION ONUTU[1], TIMUR CHIS[2], LUCIAN ION TARNU[3]
[1]Oil, Petrochemical and Environmental Engineering Department,
Oil and Gas University,
Blv. Bucuresti, nr.39, Ploiesti,
ROMANIA

[2]Oil and Gas Engineering Department,
Oil and Gas University,
Blv. Bucuresti, nr.39, Ploiesti,
ROMANIA

[3]Managing and Industrial Engineering Department,
Lucian Blaga University,
Victoriei Blv, nr.10, Sibiu,
ROMANIA

Abstract: - Some synthesis processes obtain Acid tars after treating the refining products with sulfuric acid. They are highly toxic to the environment, occupying important storage spaces. Following the closure of the refineries in Romania, large quantities of acid tars were abandoned in oil residue tanks. Currently, activities are being carried out to inventory and dispose of them. Incineration is the only possibility to treat these wastes, which release dangerous substances into the air (CO_2, SO_2). That is precisely why we tried to find solutions to treat these wastes by encapsulating them with various additives, the best solution being their physical alteration through encapsulation and stabilization in situ. The results obtained from the treatment of some acid tars taken from Romania, with additives consisting of cement, sand, calcium oxide, sodium hydroxide, bentonite, and emulsifier, are presented, the created recipes being used to treat 80 collected tar samples. The effects of these recipes on the primary pollutants are also analyzed (metal content, total hydrocarbons in oil, the number of acids, cyanides, chlorides, and sulfates).

Key-Words: acid tars, additives, pollution, oil waste, encapsulation, disposal, physical alteration.

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1 Introduction

More than 80% of petroleum waste generated in refineries is reused, regenerated, or recycled, and the remaining 20% is disposed of by an acceptable method, [1].

Oil waste, pollutes the environment and occupies important areas of arable land and constitutes, at the same time, an essential loss of materials, grafting in this way the expenses of the refinery, [2].

In these conditions, knowing the qualitative limitations related to the total content of hydrocarbons (TPH) and heavy metals of these residual materials, the analysis methods were established and discussed, later correlated with the conditioning/treatment/bioremediation options (or combined) for the preparation petroleum waste for recovery or disposal, [3].

Wastes are generated throughout the petroleum industry that include drilling fluids, hydrocarbon-containing wastewater, oil effluent, treatment plant sludge, tank bottom sludge, acid tars, spent catalysts, bleaching earth, etc., [4]

At the refinery level, the amounts of residual solid materials are within the limits of 3 to 5 kg/ton of crude oil processed, mentioning that over 80% of these residues are highly polluting because they may contain toxic organic substances and heavy metals.

For any member state of the European Union, therefore, also for Romania, the problem of eliminating oil waste and the investigation and remediation of lands historically contaminated with such compounds is a priority.

According to the national inventory of potentially contaminated sites for 165 years of crude oil refining, in 2004, there were 1183 potentially contaminated sites in Romania, of which 861 were potentially contaminated sites from the oil industry.

Up to this moment, an area of 1,054,549 square meters has been decontaminated, of which 377 oil wells and 39 mud pits represent the equivalent of 84% of the total recorded at the national level, [5].

Tars are a sludge pollution refinery and are liquid or semi-solid residues with mixed composition resulting from the carbonization of organic materials from a high-temperature process, [6].

These industrial wastes come from the refining of oils by adding sulfuric acid, thus containing sulfonated organic compounds.

They were obtained for the first time at the end of the 19th century, following the manufacture of distilled oils, motor oils, and other types of oils, by refining with concentrated sulfuric acid or with oleum, [7].

At the same time, acid tars are the result of the refining of special oils, such as transformer oil, hydraulic oil, medicinal oil, and cosmetic oil, and the production of flotation reagents and petroleum additives, individual sulfonation of some hydrocarbons and some petroleum fractions.

They are also obtained due to the alkylation of isobutene with olefins, a process necessary for the manufacture of a valuable octane component, and by treating some aromatic compounds with oleum, [8]. In England, removing impurities such as lead, zinc, and manganese from used lubricating oils using sulfuric acid resulted in acid tar of much more variable composition than benzene refining, [9].

In some processes of treating flotation reagents, a white oil is also obtained with a composition dependent on the nature of the oil, the contaminants it contains, and the amount of acid used, [10].

In the process of formation of acid tars, the following stages are identified, [11]:

A. acid tars appear emulsified in the first phase, with much less stability.

Afterward, the separation of an upper phase formed by a lighter emulsion occurs, in which the continuous phase is the petroleum product, and the dispersed phase is sulfuric acid and water.

A thin film is formed between the two phases, made of sulfonic acids;

B. In the second stage, sulfuric acid, water, and low molecular weight sulfonates form a cloudy gray-black solution containing sulfates of nitrogen compounds;

C. Over time, the upper layer of acid tars is washed away with rainwater, diluting the existing sulfuric acid. Also, the organic mass begins to oxidize due to the presence of oxygen in the atmosphere and the heating of the tar (which works as a black body and absorbs solar energy, reaching temperatures of 80 - 95ºC);

D. During hot oxidation, resinous, asphalt genic, and carbide compounds are obtained, the tar maturing and becoming a solid mass. In this stage, hydrogen sulfide releases ammonia, and sulfur oxides into the atmosphere.

For aged tars, kept for a long time in storage pits (petroleum residue storage pits) or observing the following transformations:

A. In the first stage, the formation of a layer of organic mass similar to bitumen, which can have a softening point of up to 60ºC, was found on the surface. This bituminous layer has a relatively low mineral acidity, with a composition of heavy sulfonic acids, heavy naphthenic-aromatic acids and resins, asphaltenes, carbides and carbenes, chemical products formed by polycondensation and polymerization. The presence of some metals (existing in crude oil) was also found.

In this layer, free hydrocarbons are only present in a tiny proportion;

B. The lower layer is formed in acidulated water, with dissolved compounds such as metallic sulfates and sulfides of essential compounds from petroleum products, [12].

These transformations of acid tars have as their purpose the formation of thick, viscous tars that do not separate easily and that have the property of quickly dissolving oxygen and other strongly polar components, which over time lead to polymerization-polycondensation reactions with the appearance of macromolecular compounds such as resins and asphaltenes.

Thus, the tars take on the appearance of bitumen that solidifies at the interface with the environment and hardens over time.

The range of production processes that generate tars, as well as the variations in the properties of intermediate and final compounds, make the physicochemical properties of acid tars vary significantly from one batch of petroleum products to another and even within the same batch, [13].

The presence of acid tars on a specific site/battle can have the following characteristics and ways of manifestation:

- Black or dark brown spots, signs of tar leaks or unvegetated areas;

- Degraded surface tars;
-Gaps/depressions;
-Clay/gravel/sand pits;
-Grouped areas;
-Areas with smells;
-Areas with previous fires.

Depending on the environmental conditions, its origin, and composition, the tar will have various external forms, [14].

The most common form is friable tar, usually observed on thin or isolated tar bodies that can lose their water and content of volatile organic compounds without being replenished from the bulk tar mass. This form of tar can produce dust-sized particles that are vulnerable to the wind blowing and thus migrating off-site.

In conclusion, acid tars are secondary products from refining petroleum fractions, being complex organic and inorganic mixtures with unique physical properties.

2 Possibilities of Conditioning, Treatment and Processing of Acid Tars. History and Trends

Acid tars cause environmental pollution, occupy important areas of arable land, and constitute an essential loss of valuable minerals, grafting the expenses of the refinery in this way.

That is why, since their formation, the valorization of such wastes has been attempted.

Still, the complexity of their composition led to the definition of various treatment techniques suitable for the resulting waste.

Processing of acid tars has also been attempted, yielding commercial products such as surfactants, H_2SO_4 and colloidal sulfur, desulphurized light liquid hydrocarbons, coke, and activated carbon, fuel for boilers and furnaces, pitch, asphalt and asphalt binders, compositions thermal insulation and anti-rust mastics, commercial ammonium sulfate, gypsum and cement obtained from deacidified washing water with calcium oxide or hydroxide and a mixture of acid tars with peat as a fuel with a high calorific value.

However, during the treatment of acid tars, only the top layer, which is easy to recover and process, is usually used.

From the publications in circulation, it follows that, over time, various possibilities of processing / disposing of acid tars have been tried, briefly described in what follows, [15].

2.1 Neutralization of acid tars

Neutralization can be achieved by applying quicklime (calcium oxide) directly to the acid tar, in situ, this being possible where the tar is located, in the battle, at a shallow depth.

Alternatively, the process can be carried out ex-situ, either in layers or in specially designed installations. Due to the impossibility of achieving a homogeneous mixture of calcium oxide and acid tar, neutralization becomes a cumbersome process. It is mainly undertaken as an intermediate step before the final disposal of petroleum waste. During the neutralization experiments, mixtures with different intensities/degrees were performed. Thus, the tars were mixed with earth to give a crispy, crumbly texture suitable for neutralization. Even contaminated soils from the site or from other sites that could be used for this purpose were used, the proportions achieved being 50:50 soil to tar.

Neutralization involves mixing the tar-soil mixture with lime (up to 30% lime), and the resulting neutralized tar could be stored before the current European environmental protection legislation.

As an option, the single application of acid tar neutralization has become more and more difficult because there are fewer suitable and available landfills to accept this waste, the cost being over 200 Euro/ton.

2.2 Incineration of Acid Tars

Burning, as such, is applied to types of tars that do not lend themselves to other processes or if the small volume of tars makes other processes uneconomical. In general, by burning, the volume of residues is reduced by almost 85%, and for storing the ash resulting from the burning of one ton of residue, an area of only $0.1 m^2$ is required.

Viscous and semi-solid tars could be burned in hearths with mobile feeding grates mixed with coal or spent absorbent earth, the process being disturbed by:

a. The appearance of corrosion at the burners, pipe screens, and ovens' masonry;
b. Pollution of the atmosphere with gases containing sulfur dioxide and trioxide.

2.3 Thermal Decomposition

The thermal decomposition of acidic tars containing water is one of the oldest processes. Depending on the types of tars, fluid or semi-fluid residues and diluted sulfuric acid (30 - 40%) can be obtained, with a content of unstable organic compounds corresponding to 1.5 - 4% carbon, compared to pure sulfuric acid.

In principle, the thermal decomposition takes place at temperatures of 260 - 650ºC, involving the reduction of free sulfuric acid to sulfur dioxide and water, with the help of the hydrogen contained in the organic substance from the tars.

At the same time, the cracking of the organic substance takes place, resulting in light and complex, volatile hydrocarbons and coke with a 7-8% sulfur content.

Generally, tars with a sulfuric acid content of about 50% are suitable as raw materials.

Thermal decomposition at high temperatures was also used in practice, which is achieved by completely burning tars to sulfur dioxide, carbon dioxide, and water in cylindrical hearths where ordinary fuel is also burned to maintain the temperature at approximately 1000 - 1200ºC.

The heat is recovered partly by preheating the combustion air and partly by the method applicable for tars with a sulfuric acid content of over 75%.

2.4 Recovery of Sulfonic Acids

The organic substance in the tars may contain recoverable sulfonic acids found in the solution in the petroleum fraction and in the acid tars.

Considering the particular interest of the industry in sulfonic acids and sulfonates, many attempts have been made to recover them.

In the 80s, the possibility of obtaining coke through the thermal decomposition of tars and activated carbon used in adsorption cartridges from gas masks was studied.

At the beginning of the second decade of the last century, acid tars were neutralized with calcium oxide or sodium hydroxide, and two organic masses called NaDOS and CaDOS were obtained, which were used to cover communal roads, [16].

Next, after the 60s of the last century, the acid tar hydrolysis process was developed.

Another direction was using the acid tars from the battles to manufacture bitumen and obtain heavy fire fuels.

Modern technologies for the elimination of acid tars, applicable to other petroleum wastes, are the following, [17]:

- Pyrolysis at high temperatures (800–1200ºC) producing H_2SO_4, heat, coke with high sulfur content and activated carbon;
- Decomposition at low temperatures in the range of 150–350 ºC, followed by the production of bitumen;
- Hydrolysis with water or steam producing diluted H_2SO_4 and combustible components;
-Neutralization with various agents such as surfactants.

A reasonably advanced study, but not applied in practice, was the one in which acid tars would have been introduced into uranium mines to obtain rock specific to the uranium deposit, [18].

The non-application was due, on the one hand, to the difficulty of transporting the acid tars and, on the other hand, to the closing of the mine in the later phase. The problem of the processing/elimination of acid tars is always current, and countries with highly developed industries and clear legislation have almost completely solved this problem.

3 Experimental Strategies

The environmental impact analysis of acid tars was carried out through the following research stages, [19]:

a. Documentary study from specialized literature regarding petroleum residues/waste that can contaminate the soil, physical and chemical properties of the various categories of residual materials that can influence the quality of the soil, concerning current national and global methods for the evaluation of petroleum hydrocarbons from soil and legislative basis at the EU level and in Romania;

b. Field study carried out during three years of investigations in different areas polluted with crude oil and petroleum residues/wastes, areas related to Prahova refineries. A representative battle was taken from these areas/battles, and more than 80 soil samples were taken and analyzed in different stages of the experimental studies.

c. Preliminary or detailed experimental studies regarding the characterization and evaluation of options for identification, analysis, treatment, and possible valorization of some petroleum residues/wastes, [20].

d. The laboratory studies for samples of oil residues/waste taken from the sites where this waste is stored included a series of complex and complementary analyses to establish the composition, physical and chemical properties that can influence their behavior towards the storage environment, data that provide the information necessary for further processing/elimination, [21].

e. Study of statistical processing of experimental data by using artificial intelligence and Data Science to predict the properties of acid tars from battles and the associated leachate. The Study will follow the initial data processing, selecting the appropriate modeling algorithm, and calculating its estimation accuracy, [22].

To estimate the properties of new acid tar samples without testing them, we have created a computer tool that helps the user in this regard.

It was written using the Python programming language, version 3.9.7, and the PyCharm Community Edition programming environment, version 2021.2.3.

They are free and can be downloaded from the manufacturers' websites, [11].

The computer tool created uses mathematical modeling and data science techniques to estimate the following nine properties of acid tars sampled from the GA battle:

-initial pH of the acid tar sample;

- The THP content of the acid tar;

-The initial concentration of lead in the acid tar (mg/kg);

-Initial cadmium concentration (mg/kg);

-Initial concentration of copper (mg/kg);

- Initial concentration of chromium (mg/kg);

- The concentration of nickel in the acid tar (mg/kg);

-The initial concentration of arsenic in acid tar (mg/kg);

-The initial concentration of cyanides (mg/kg).

The nine properties presented above form the independent variables (or predictor variables), and the sampling depth is the dependent variable (or response variable).

The following quantities are used as predictor variables:

-X and Y coordinates of the points from which the soil samples were extracted (stereographic projection 70 is used as a representation system for these coordinates);

-The depth from which the acid tar samples were extracted (cm). These samples were taken from either the 0.3 or 0.5 m depth.

The working algorithm of the developed program has the following steps:

-Loading the raw data from the Excel file;

-Determining predictor variables (input data) and response variables (output data) and selecting them from the uploaded data;

-Dividing processed data into training data and test data;

- Selection of the appropriate mathematical model for the available data;

- Application of the mathematical model selected in the previous step;

-Testing the estimation accuracy of the chosen mathematical model.

Within the developed program, cross-validation was applied to the forest of decision trees, resulting in prediction equations of the form:

$$y = a_0 + a_1 x_1 + \cdots + a_n x_n + \varepsilon \qquad (1)$$

Where y represents the dependent variable (or response variable), and x_i represents the independent variables (or explanatory variables).

The coefficients a_i are calculated by the linear regression algorithm so that the sum of squared errors is minimal.

Among them, the coefficient $a0$ is constant and is called the intercept.

The variable ε holds the approximation errors of the model.

4 Materials and Methods

The optimal application of the processing, recovery, or treatment/disposal methods of petroleum residues/waste requires a thorough knowledge of their chemical composition.

The potential valorization or correct disposal of petroleum waste, especially those in the acid tars, in conditions of proper preservation of the physical environmental factors (air, water, and soil), is based on applying a research methodology that includes methods and equipment suitable analysis.

The characterization of waste and oil residues, but also the final treated products, was achieved by determining the following key indicators: pH, THP content, metals, chlorides, Dissolved Organic Carbon (COD), Sulphates, Total Dissolved Solids (TDS), Carbon Total Organic (TOC).

According to Ord 95:2005 – Establishing acceptance criteria and preliminary procedures for accepting waste for storage and the national list of waste accepted in each class of landfill to be stored and accepted in landfills, waste must meet specific characteristics chemicals.

That is why specific analyses were carried out for the acid tars studied and treated.

Also, the validation of the treatment process by stabilization-encapsulation of acid tars required the performance of the leaching test, consists of bringing the waste sample into contact with a leaching agent (water) at a certain waste/leaching agent mass ratio (L/S=2 l/kg or L/S=10 l/kg), keeping in contact for 24 h, separating the leachate and analyzing the obtained eluate to determine the quality indicators pursued.

Analytical determinations were made according to the following standardized methods:

- SR EN ISO16703:2011 – Soil quality. Determination of the hydrocarbon content in the C10–C40 range by gas chromatography
- SR EN 16192:2012 – Characterization of waste. Leachate analysis
- SR ISO 11465:1998 – Soil quality. Determination of dry substance and water content relative to mass. The gravimetric method
- SR EN ISO 9377-2-2002 – Water quality. Determination of the hydrocarbon index
- PSL 70 SR EN ISO 15586:2004 - Water quality. Determination of lead content. Atomic absorption spectrophotometric method with graphite furnace
- SR ISO 10523:2009 – Water quality. Determination of pH.

To demonstrate the chemical composition and compositional diversity of this particular waste, the acid tars from a separate area, different from the storage tank of a refinery, were investigated.

The analyzed acid tar pit has an area of 6 ha and was established in 1960.

It comprises 15 smaller pits initially designed to store residues resulting from crude oil extraction. Later, residues from refining petroleum products were also deposited here.

An estimated 80,000 m^3 of waste (acid tars, oil residues, and acid water) is stored in the analyzed refinery tanks, and until now not to decontaminate these tanks (Table 1).

In addition to the metal content, the amount of organic and inorganic products, water content, sulfur, and acidity were determined.

In addition, the percentage content of the organic part was analytically determined: the content of saturated hydrocarbons, aromatics, resins, and asphaltenes (SARA analysis).

The physicochemical analysis of an acid tar taken from the refinery analysis battle is presented in the tables below:

Table 1. The physico-chemical analysis of tar acid

Properties	Gasoline acid tar	Petroleum acid tar	Medium lubricating oil
Density, kg/m^3	1,6	1,4	1,2
Total acidity, % mass	55,4	45,8	18,3
Sulfuric acid H_2SO_4, % mass	46,0	33,2	17,3
Water content, % mass	3,3o	5,6	3,8

Properties	Value interval
Moisture	9 - 15 %
Ash	1 - 5 %
Acidity	15 - 40%
Organic matter	40 - 75 %
Lower calorific value	23550 kJ/kg
Density	1220 kg/m3
Flammability temperature	120 - 160 0 C

5 Treatment of acid Stabilization/Encapsulation Tars

Stabilization/encapsulation treatment of inorganic contaminants has been practiced for decades and is supported by many studies, but much less information is available on its use on organic compounds.

Currently, the cement-based stabilization/ encapsulation treatment of organic contaminants is classified into three categories:
-direct immobilization of organic contaminants,
-immobilization of organic contaminants after adsorption,
-immobilization of organic contaminants using oxidizing/reducing agents, [5].

The hydration acceleration efficiency of different cations is $Ca_2^+ > Mg_2^+ > Sr_2^+ > Ba_2^+ \sim Li^+ > K^+ > Rb^+ \sim Cs^+ > Na^+ > NR_4^+ > H_2O$, where NR_4^+ means the quaternary ammonium ion and H_2O means the absence of the additive.

The published results indicate that:
-calcium has the highest efficiency,
-efficiency depends mainly on the charge and size of the ion, the most efficient being the process with minor, highly charged ions, [5].

For highly soluble calcium salts at the same equivalent concentration, the order of anion effectiveness is $Br^- \sim Cl^- > SCN^- > I^- > NO_3{}^- > ClO_4^- > H_2O$, which shows a similar trend to that of cations in terms of size ions.

It should be noted that salts of Zn, Sn, Pb, soluble phosphates, and fluorides delay the hydration process, and inorganic salts that form complexes with calcium also act as inhibitors.

The efficiency of treatment by the stabilization/encapsulation process of organic contaminants can be improved by using adsorbents for the organic components.

Such adsorbents can be incorporated as additives in the cement mixture or pretreatment before conventional cement-based solidification.

These additives (residual products of industrial processes, such as activated carbon, shredded tire particles, and organic clays) can increase the chemical containment of the contaminant.

Additives such as silica fume and fly ash can improve the physical retention of organic compounds by reducing the porosity and permeability of the waste form.

Activated carbon is commonly used in the remediation of organics and for capturing many heavy metals.

The use of activated carbon as a pretreatment adsorbent in stabilization/encapsulation technology has yet to be widely reported, probably due to high costs, but the use of activated carbon in stabilization/encapsulation technology will expand because it can be achieved by using regenerated activated carbon.

In study reported a reduction of organics concentration to a target level in leachate by stabilization/encapsulation treatment of organic contaminants such as creosote, dioxins, and pentachlorophenol (PCP) using cement formulations containing activated carbon or other proprietary reagents at the site American Creosote of Jackson, TN, [1].

Also, organophilic clays (bentonites, hectorites), modified to be hydrophobic, with an affinity for insoluble organic substances, can act as promising adsorbents for organic contaminants and allow them to be treated by cement-based solidification, [3].

Modifying clays by exchanging natural cations (Na^+, K^+) with organic cations significantly improves adsorption capacity compared to unmodified clays.

The water solubility of the contaminant diminishes the effectiveness of organophilic clays in immobilizing organic contaminants because organic molecules adsorb on the organophilic clay surface by hydrophobic attraction, which is more favorable when the compound is less soluble in water, [4].

The immobilization of organic compounds in a cement matrix, with or without adsorbent, is mainly the result of physical blocking.

Long-term effectiveness for immobilizing organic contaminants can be achieved by converting organic waste into less hazardous hydrocarbons.

This leads to a combined process (contaminant immobilization and degradation).

Data on the long-term performance of applying stabilization/encapsulation technology at hazardous waste sites are generally limited.

The environment and long-term conditions to which the solidified waste is exposed can affect the stability of the treated waste.

Stabilized cement-based wastes are vulnerable to the same physical and chemical degradation processes as concrete and other cement-based materials; that is, they have the potential to disintegrate for 50 to 100 years.

EPA's Eleventh Status Report on Treatment Technologies Used at Superfund Sites shows that encapsulated and immobilized pollutants has been implemented at 24% of sites to metal contamination (174 sites) and organic substances (129 sites), [11].

Current stabilization/solidification systems can be grouped into the following seven process classes:
- Solidification by adding cement,
-Solidification by adding lime or other pozzolanic materials,
- Embedding waste in thermoplastic materials such as bitumen, paraffin or polyethylene,
-Heat-resistant micro-encapsulation,
-Macro-encapsulation of waste in an inert layer,
-Treatment of waste to produce a cement product with the majority of additions of other constituents,
-Forming a solid mixture by fusing waste with silica.

It can be noted that the first two methods are the most frequently used, being suitable for the vast majority of inorganic process waste.

Treatment costs for the other processes are generally higher; the latter techniques are applied to problematic waste, such as radioactive waste or those with a high organic content.

6 Applicability and Stage of Development of Stabilization/ Encapsulation Technology

The stabilization/encapsulation technology is a full-scale commercial technology, and its application presents the following particularities, [11]:
-stabilization/encapsulation demonstrated its effectiveness for inorganic contaminants, mainly metals and radionuclides, in the presence of a low level of organic materials
-inorganic salts can affect the setting rates of cement, reducing the strength of the stabilized product
-stabilization/encapsulation is typically applicable for situations where the organic content of the waste/soil, as measured by total petroleum hydrocarbons (TPH), is more significant than 5,000–10,000 mg/kg, as in some cases, the material has leached from the cement matrix over several years:
-the presence of organic contaminants, especially VOCs, makes the use of stabilization/encapsulation ineffective,

-organic contaminants can volatilize due to the heat generated during the reaction (leading even to the need to obtain air emission permits),
-the toxicity of the contaminants in the sediment does not change,
-the addition of activated carbon and other adsorbents allows the application of the stabilization/ encapsulation process at higher content of organic substances in the treated tar,
-anions can also be immobilized by trapping or microencapsulation,
-erosion and diffusion processes can favor the release of contaminants,
-fine particles can bind to larger particles, preventing the binder from binding effectively,
-the high degree of humidity of the treated tar influences the application of the stabilization/ encapsulation process (requires increased amounts of reagents),
- Long-term monitoring is required after applying the stabilization/encapsulation process.

7 Standards of Remediation, Assessment and Safety. Long-term Maintenance of the Application of the Stabilization/Encapsulation Process. Remedial Standards

To establish the objectives regarding the remediation of the contaminated site, there are two general approaches based on:
-Guidelines or criteria (guidelines and recommendations),
-Risk assessment (the risk presented by contaminants both to humans and to the ecological system),
-With the risk-based approach, each site is assessed separately.

Factors such as contaminant type and concentration, as well as possible receptors and routes of exposure, are considered, and appropriate concentration limits for individual contaminants are then set site-specific, [10].

It should be noted that the relative proportions of waste and other constituents that make up the "mix" subjected to the stabilization/encapsulation process vary considerably depending on the composition and nature of the waste/acid tars, determining the particularities of the application of the technology.

If the most appropriate process is selected for a given situation and a given waste stream, subsequently published information will likely be of little help, [11].

Hence, a detailed evaluation of the stabilization/encapsulation process in the laboratory is imperative.

In addition, it is necessary to carry out specific laboratory tests on each waste stream to be solidified in a specific facility and according to a specific recipe.

The effectiveness of a stabilization/solidification process for a particular waste is correlated and determined according to three main properties of the treated waste: treatment or curing time, physical properties, and resistance to leaching (solubilization) of hazardous components, [11].

Physical properties such as density and compressive strength of treated waste are essential when determining its suitability as a material for land remediation.

The treated waste's permeability affects the resistance to the leaching of hazardous components, which controls the rate of penetration of the leaching fluid and the rate of leaching of contaminants into that fluid.

The stabilization/encapsulation process is the most viable technology for containing contaminated soils and other hazardous wastes that cannot be economically destroyed by chemical, thermal, or biological means.

Unfortunately, published data to verify the performance and durability of treated waste stored in landfills over time are scarce and sporadic, although research shows that the same environmental concerns that affect the durability of concrete must be considered when evaluating the durability and permanence of tar acid-based cement.

In these evaluations, leaching tests and chemical analyses should be followed by microscopic analyses that would supplement the data to establish the long-term performance of the stabilization/encapsulation process technologies.

Future use of the remediated site and environmental conditions (natural weathering) may erode the materials used for contaminant stabilization, affecting their ability to immobilize contaminants.

Wastes stabilized by the cement-based stabilization/encapsulation process are vulnerable to the same physical and chemical degradation processes as concrete and other cement-based materials, [11].

It should be noted that the material treated by the stabilization/encapsulation process uses concrete differently from the conventional one in construction; the design of the mixture is based on the properties of the contaminated environment that is being treated.

Economic analysis of the stabilization/encapsulation treatment costs also includes the transportation of raw and stabilized waste, the necessary equipment, and labor costs.

Capital and installation costs for inorganic fixing processes depend on the scale and degree of complexity of the work required on site.

8 Validation and Monitoring

The validation of the applied remediation process is based on and involves the same principles for the remediation of acid tar sites as for other contaminated sites.

In the case of strategies involving the removal of acid tars for authorized off-site disposal or incineration (regardless of whether or not pretreatment is carried out), it will be necessary to verify that the removal action has met the agreed criteria, [10].

This will typically involve sampling at the base and edges of any excavation to confirm the degree and extent of any contamination associated with random sampling in other areas.

If groundwater needs to be remediated (for example, if there are loose petroleum products), groundwater monitoring will be required at appropriate locations around the tar pit.

Monitoring will be required before, during, and after remediation until the risks are appropriately managed and until a valid statistical data set has been produced that demonstrates that the concentrations are within the limits and that the evolution trends are acceptable.

Current legislation stipulates that any remediation be associated with a post-remediation monitoring plan - documentation in which the post-remediation activities are described, to verify the achievement and maintenance of the proposed remediation targets and objectives at the end of the remediation, respectively the evaluation of all components of the remedied geological environment.

9 Research on the Treatment of Contaminants by Applying the Stabilization/Encapsulation Process. Assessment of the Risk due to Acid Tars

The published investigations summarize the mechanisms involved in the immobilization process of As, metals (Zn, Cr, Cu, Pb, Cd, etc.), and PAHs and present the specific results from laboratory and field experiments obtained by applying the stabilization process/ encapsulation.

Toxicity Characteristic Leaching Procedure (TCLP) applied to sludge containing solids using four different binder systems consisting of cement mortar, fly ash, clay, and lime and cured for 28 days showed that the volume of sludge added, which resulted in maximum metal stabilization was 60% for all combinations, above which the metal fixation efficiency decreased, resulting in high zinc values in the leachate.

In the immobilization of Cd by stabilization/ encapsulation process technology using a mixture of sand, cement, and clay, it was found that clay increased the metal absorption capacity.

In contrast, sand and cement improved the compressive strength, [11].

Exciting experiments were devoted to studying the mobility and availability of metals stabilized by using zeolites in contaminated soils.

The amount of dissolved Cu, and thus its mobility, was strongly reduced, and the percentage of metal-stabilized in the solid phase increased over time, reaching values of 30 and 40% at 30 and 60ºC, respectively, after fixing, [11].

In addition to the publication of specific, particular cases, current knowledge in the field of cement within the stabilization/encapsulation process is also disseminated, focusing on the chemistry of cement, the effects of inorganic and organic compounds on cement hydration, and the immobilization mechanisms of different organic and inorganic compounds.

For the treatment of organic contaminants, using adsorbents such as organophilic clay and activated carbon, either as pretreatment or as additives in the cement mixture, can improve the immobilization of waste contaminants.

It has proven effective in immobilizing organic contaminants related to activated carbon but is generally too expensive for routine use.

A study on the use of powdered activated carbon to prevent leaching of organics from solidified/stabilized waste forms showed that the addition of 1% activated carbon reduced the leaching of some organic contaminants (phenol, 2-chlorophenol, chlorobenzene, aniline, and methyl ethyl ketone) by more than 70%.

In comparison, an addition of 2% contributed to a reduction of less than 1% for most organics, [7].

Various studies note that the degradative stabilization/encapsulation variant, which combines chemical degradation with the conventional stabilization/encapsulation process, is promising. However, further studies are needed to assess its technical and economic feasibility.

Acid tars can threaten human health and the environment due to their acidity, volatiles, and other hazardous components.

Tar acid spills can occur through direct contact, outgassing, off-site bulk migration of tar, and contamination of surface and groundwater, [8].

The leaching and migration phenomena of acid tars associated with natural weathering have demonstrated that acid tars can leach significant levels of contaminants if disturbed. In contrast, the level of leaching is significantly lower in the water table. Public risk perceptions of acid tar deposits may diverge from anticipated reactions and professional risk assessment. How the public perceives contamination risks is essential to managing contaminated sites. Although the public is generally unaware of the chemical composition of tar acids and their associated risks, those who live near sites contaminated with tar acids can "familiarize" themselves with constant pollution.

In addition, the experience of low probability and delayed-effect risks—such as health effects from contamination—tends to produce an underestimation of the risk presented.

In this context, the acid tar battle can be seen, visited up close, etc., without any visible adverse effects. This experience may lead people to feel the need to ignore experts' warnings about the dangers of tar acids.

Taking into account (the risk of accident), in particular, the substances used and the technologies used, from the point of view of security, the remediation of acid tar battles involves several risk factors, [12]:

- The content of the battles,
- Potential VOC and SO_2 emissions,
- The instability of the battlements' dykes,
- The possible presence of other deposited dangerous materials (e.g., unexploded wartime ammunition),
- Nearby pipelines with flammable and explosive products,
- Human settlements in the vicinity, with some houses located right next to the fence of the refinery, in the area of the battles,
- Carrying out other economic activities in the area of remediation.

To work safely in the application of the remediation methods of acid tar battles, it is necessary to act in stages, according to the hierarchy of prevention: risk reduction, collective protection measures, personnel protection measures, personnel training, instructions, and means of prevention.

10 Additives used for the Stabilization/ Encapsulation of Acid Tar

Based on literature data and consultation of published patents [US 20140249346, US5700107, US20140249346, EP0655493, US5049256, GB1501572, US20140249346, US5700107, US20140249346, US5700107, EP1868747 EP1868747, US2012253094, US5049256, GB1097565, GB150157], for treatment by the method of stabilization/encapsulation chosen and applied to acid resins, the following substances were used as additives and filler materials: cement, sand, calcium oxide, sodium hydroxide, bentonite, emulsifying detergent, strengthening additives, absorbent, and sodium metasilicate.

The rest, up to 100%, is represented by acid tar subjected to stabilization.

Potentially applicable reagents were identified before lab-scale treatability testing.

Identifying the potentially applicable reagent depends on several factors, including the contaminant being treated, the concentration of contaminants in the acid tar, the geotechnical and tar properties, required performance parameters, and minimum acceptable performance criteria for the treated tar.

The identification and practical choice of the reagents applied in the experiment were based, on the one hand, on the consultation of the technical literature carried out in the theoretical research and, on the other hand, on the author's experience in the implementation of stabilization/encapsulation projects.

Several candidate reagents were thus identified, narrowing down the number of reagents based on low-cost and less time-consuming treatability tests.

The selection of candidate reagents was based on the knowledge and analysis of chemical interferences and incompatibilities of the chemical behavior of the metals in the tar, but also taking into account the cost and history of the process.

The composition for neutralization, stabilization, and encapsulation of acid tar with TPH values below 200,000 mg/kg and DOC below 1000 mg/kg dry substances., according to research, is represented in the adjacent table (Table 2).

Table 2. The composition for the neutralization, stabilization, and encapsulation of acid tar

Component	**(%)**
Cement	3-20%
Sand	2-5%
Lime	3-8%
Sodium hydroxide	1% - 10%
Bentonite	1-2,8%
Emulsifying detergent	1-2%
Strengthening additives	1%

Sodium metasilicate was added in proportions ranging from 0.3 to 0.8%.

As argued in the literature, the final performance of the stabilization/encapsulation technology application is determined by the quality and intrinsic properties of the additives and binders in the treatment recipes.

The ordinary Portland cement (CPO) used in the present study allows the immobilization of Cr, Cu, Zn, Mn, and Pb.

The addition of cement leads to an increase in the degree of immobilization with an increase in the curing time of the hardened material. This reference is attributed to the pozzolanic or pozzolanic/hydraulic properties of the cement on the microstructure of the hardened material. Additives added to cement and the hydration reactions in the mixtures favor the formation of the specific microstructure, favoring the immobilization of dangerous elements.

The sand is used as an additional aggregate that forms a hard layer covering tar contaminants in the presence of cement and water.

Calcium oxide (slaked lime, quicklime), presented as a white powder, was used to neutralize acid tar. In addition to the neutralizing effect, the calcium oxide and the emulsifier contributed to the transition of the metals from the volatile phase to a stable phase.

The added lime favors the immobilization, especially of Cd, Cu, Ni, Pb, and Zn.

Sodium hydroxide neutralized the tar, and the reaction was strongly exothermic.

The emulsifying detergent stabilizes the pH and obtains a homogeneous mixture of the stabilized tar. By breaking the hydrocarbon chains and embedding the ingredients faster and deeper, the presence of the emulsifying detergent leads to a higher degree of encapsulation of the tar.

To mix and incorporate all the ingredients proposed in the recipes elaborated in the thesis, in a short time, the emulsifying detergent was used according to the Brand Registration Certificate no. 107443, granted by the STATE OFFICE FOR INVENTIONS AND TRADEMARKS.

Bentonite and cement contribute to the hardening/encapsulation of the acid tar and the additional retention of Pb.

The absorbent is used to reduce the volume of the treated tar.

The added sodium metasilicate had a water-scavenging effect. Sodium metasilicate is not a cleaning agent per se but is a strong base that reacts violently with acids. It was added to elaborate recipes because it maintains the added emulsifier's and absorbent's cleaning efficiency, mainly by inactivating water hardness.

It has also been reported that Cu can bind cement using this agglomerating agent, sodium metasilicate, $Na_2SiO_3\ 9H_2O$.

The freshly prepared tar sample is homogenized, and binders are added to stabilize and encapsulate the acid tar.

After completing the treatment in the laboratory, the stabilized tar is presented as a compacted block.

The values of the pollutants identified in its leachate fall within the maximum values allowed according to Order 95/2005.

The final processing and verification found that a stabilized and encapsulated material with low permeability, low leachability, and moderate to high resistance was obtained, which meets all the performance criteria.

The volume of the treated tar shows an increase of up to 5% of the initial volume of the acid tar before treatment.

This aspect is essential in the further valorization stage of the research because it will allow the tar to be treated in situ, using only the limited space of the existing pits, without digging additional pits to store the surplus resulting from treatment.

Since acid tar is a particular waste, its treatment by stabilization/encapsulation had to be carried out carefully (see the literature study).

First, being unstable from a geotechnical point of view, it can show creep effects depending on the type and temperature.

Secondly, leaks of organic compounds (hydrocarbons) and inorganic compounds (sulphuric acid, metals) can be recorded in contact with water.

After adding and mixing the additives, no significant heating of the neutralized and treated acid tar, leading to volatilization of specific contaminants, was observed.

Also, no sulfur dioxide emissions were detected since it was an "old" tar. Since it was not intended that the tar thus treated and stabilized be exploited as a construction material, in the thesis, it was not analyzed from a geomechanical point of view. Contaminants once immobilized in the matrix, do not migrate as long as the integrity of the matrix is maintained. The leachate from the disposal site was analyzed to monitor any contaminant migration.

As mentioned, from the field under study, acid tar samples were taken, and their composition was determined, following the following indicators: pH, THP, metals, cyanides, chlorides, DOC, and sulfates and were compared with the imposed limit values by Order no. 95/2005.

For all locations, the depth of acid tar samples was within the range of approx. 5-30 cm.

11 Formulation of Stabilization/ Encapsulation Treatment Recipes

Given the high values above the legal limits of the mentioned indicators, several recipes were formulated, prepared, and tested, of which three representative recipes were retained in the end. After each recipe, several different portions of acid tar were mixed and tested. The samples were tested for the curing process as a function of time by visual examination and portable penetrometer tests. The testing process was stopped for recipes that did not show good results. As a result of the limited success in earlier tests, the additives were dried and mixed in subsequent tests (Table 3).

The three formulated recipes stand out for:

- Constant concentrations of strengthening additives, absorbent, and sodium hydroxide (approx. 1% each)
- Variable amounts of emulsifying detergent, produced by Eurototal (1; 3.5 and 4% respectively)
- Increase in cement concentration (from 3% in recipe 1 to 8% in recipe 3)
- The added calcium oxide varies from a concentration of 8% in the case of the first recipe to 7% in the formula of recipe 3
- Increasing the concentration of bentonite (from 1% in recipe 1 to 2.8% in recipe 3)
- A relatively constant increase is noted for sodium metasilicate (0.30%, 0.50%, and 0.80%, respectively - recipe 3).

Table 3. The representative recipes for treating the acid tar tested

Compound	Recipe 1	Recipe 2	Recipe 3
Sodium metasilicate	0,30%	0,50%	0,80%
Emulsifying detergent	1%	3,5%	4,0%
Lime	8%	3,00%	7,00%
Magnesium oxide	0,1%	0,2%	0,3%
Bentonite	1%	2%	2,8%
Sand	2%	5%	3%
Cement	3%	5%	8%
Strengthening additives	1%	1%	1%
Absorbing	1%	1%	1%
Sodium hydroxide	1%	1%	1%

For tars with high pH and low THP values, recipe 1 applies. Recipe three is used for cars with low pH values and high THP values. For tars with medium TPH values, recipe 2 gave the best results.

It was found that THP and pH values and other indicators, including the concentrations of various metals in the initial tar, influence the efficiency of the recipe used.

Therefore, if the application of the chosen recipe did not decrease concentrations below the limits provided for in Order 95/2005, one of the other two recipes is used.

The third recipe is used if even the second recipe does not give the expected results. All these attempts were completed by obtaining two patents, one international and the other national. After applying the recipes according to the inventions, a significant decrease in the parameters was found, and compliance with the norms provided by Order No. 95/2005.

12 Conclusion

The analysis and discussion of the experimental data led to the following conclusions:

The pH. The pH values measured for the acid tar stored in the studied area range from 0.20 to 5.20.

The strongly acidic character has intensified, from the already acidic character of the categories of potential waste stored in the studied area (sludge, oil sludge with pH values between 3.9 and 5.6) to that due to the mixture of these wastes with the tar acid.

The TPH (total hydrocarbons in soil) values vary at different depths within the same plot, with a slight tendency to decrease in depth from the soil surface, with 61 samples out of 82 having a higher concentration of TPH at a depth of 30 cm.

Specifically, according to the analyses, the THP of the unstabilized acid tar is between 48,333 and 477,062 mg/kg dry substances, with 59 samples with TPH content values lower than 200,000 mg/kg dry substances.

The highest concentration of TPH detected for all acid tar samples was 477062 mg/kg dry substances, which indicates the highest level of actual contamination in a sample corresponding to a depth of 5 cm.

The concentration of TPH decreased for the same point, at a depth of 30 cm, by about four times.

The study of TPH concentrations under the conditions of the application of large-scale application of cement-based stabilization/ encapsulation technologies to inorganic waste, including metal, is essential in the conditions in which it has been reported that organic substances can be easily leached.

Unfortunately, little information is available on organic leaching from acid tars after applying stabilization/ encapsulation technology or on the effects of organics on complex setting reactions, which can result in an altered cement matrix.

It was found that the films formed by asphaltenes are resistant to acidic environments (low pH) and become less persistent as the pH increases.

In the alkaline environment, these films become very weak, unstable, or even move into a mobile state. Films formed by resins are more vital in basic environments and weak in acidic environments.

Metal content

As stated, the acid tar samples were digested with nitric acid to make the metals available for determination.

The concentrations of the analyzed metals were established according to the Analysis Method SR EN ISO 15586:2004: Determination of trace elements by atomic absorption spectrometry with a graphite furnace and the method for the rapid detection of trace elements.

The equipment used was the Atomic Absorption Spectrometer with a graphite furnace and the Mobile EDXRF Device with X-ray detection to detect trace elements rapidly.

The different and, of course, sometimes high levels of metal concentrations in the untreated acid tar samples can be attributed to the concentrations of such metals in the wastes stored in pollution areas, in the additives used in the refining processes, the absorption of metals from the storage tanks and the supply, the natural presence of metals in the parent rock from which the crude oil was extracted and even in the materials with which the stabilization/encapsulation is carried out (e.g., cement).

Pb (lead). The value of 50 mg/kg, the legal limit of Pb (lead) in the soil, was exceeded for 81 samples (out of a total of 82); 11 samples have a Pb (lead) content higher than 500 mg/kg (of which four samples exceeding 1000 mg/ kg), and the rest having a Pb (lead) content between 42 and 478 mg/kg.

The Pb (lead) concentrations analysis shows a strong infestation of some samples collected from the depth of 5, where the maximum value of 2235 mg/kg was reached.

Cd-Cadmium concentrations in untreated acid tar are between 1 and 126 mg/kg dry substances; 72 samples exceed the limit value of 5 mg/kg, four samples with concentrations above 50, and 2 samples with concentrations above 100 mg/kg.

The copper (Cu). The concentration of copper (Cu) varies between 2.6 and 789 mg/kg of dry substances, with the only critical point being a level much higher than the legally imposed value of 100 mg/kg.

Chromium (Cr). For the total chromium (Cr) content, the legal limit value is 70 mg/kg, and the total chromium (Cr) content determined in untreated acid tar varied between 3 and 452 mg/kg dry substances.

Nickel (Ni). With a content variation from 2 to 859 mg/kg, 40 mg/kg is exceeded only in three points where very high values are recorded, of 859 and 528 (for depths of 5 and 30 cm). Seventy-four samples from 82 samples have values lower than 20 mg/kg.

Arsenic (As). The content of Arsenic (As) in the 82 samples of untreated acid tar varies from 1.4 to 589 mg/kg.

For Arsenic (As) content, the allowed value of 25 mg/kg provided for in Order 95/2005 is exceeded for 52 samples.

As a general finding, it is noted that the values determined and recorded for the concentrations of metals ***Pb+Cd+Cu+Cr+As***.

However, in the initial acid tar, their values were above the maximum allowed limits; in the leachate stabilized at one day, they recorded low values, some even below the quantification limit of the determination methods.

13 Leachate Analysis and Evaluation. Analysis of Eluates

The leachates were prepared and analyzed from the treated acid tars according to the leaching procedure SR EN 16192:2020 Waste characterization—analysis of eluates.

The pH. The analysis of the eluates to determine the acidity according to SR EN ISO 10523:2012 pH determination. As a general remark, it was found that increasing the pH from values between 0.2 and

5.28 (untreated acid tar) to values from 8.7 to 10 (the case of the leachate) had a beneficial role in increasing the leaching performance (e.g., in the speciation of metal contaminants).

The **TPH (total hydrocarbons in soil)** content, corresponding to the leachate, was determined by Method: SR EN ISO 9377-2-2002—determination of the Hydrocarbon Index.

The stabilization-encapsulation technology, applied in the study for the treatment of acid tar, confirmed the fact that the organic materials - hydrocarbons do not react with the inorganic binders from the three applied recipes due to the significant differences in hydrophobicity and polarity between the organic contaminants and the organic binders.

In many cases, this could lead to ineffective immobilization of hazardous organic hydrocarbon contaminants in the solid matrix and significant leaching of many contaminants.

However, the final results of the leaching tests showed good efficiency in reducing the **TPH (total hydrocarbons in soil)** content in the leachate

Metals. The concentrations of metals from the Pb+Cd+Cu+Cr+As group were also monitored in the leachate, and the following were mainly found:

- The leachate preparation and analysis were done according to SR EN 16192:2020 waste characterization. Analysis of eluates.

The leaching of heavy metals is the main reason stored acid tars and managed encapsulated/stabilized products should be classified as hazardous waste.

- The Ordinary Portland cement (CPO) used in the present study contributed to the immobilization, in particular, of Cr, Cu, Zn, Mn, and Pb. The addition of cement leads to an increase in the degree of immobilization with an increase in the curing time of the hardened material. As a result of the high pH of the cement, the metals are retained in the form of insoluble hydroxide or carbonate-type salts from the hardened structure.
- In addition to the neutralization effect, the calcium oxide and the emulsifier in the formulated recipes contributed to the transition of the metals from the volatile phase to a stable phase. The added lime favors the immobilization, especially of Cd, Cu, Ni, Pb, and Zn.
- Studies have shown that lead, copper, zinc, tin, and cadmium will likely bind in the matrix by chemical fixation, forming insoluble compounds. At the same time, mercury is predominantly retained by physical microencapsulation. On the other hand, organic contaminants interfere with the hydration process, reduce the final strength, and are not easily stabilized, delaying the formation of the crystalline structure and resulting in a more amorphous material. Reducing the interference of organic contaminants with cement hydration and improving stabilization can be done by incorporating modified and natural clays or sodium silicates into the stabilizing mixture with the cement.
- The different elements in the formulated recipes presented different leaching potentials correlated with the curing period, the compositions of the binders, and the initial and final pH, suggesting that the preliminary release behavior of each contaminant metal should be considered for the practical immobilization of the contaminated materials.
- The applied encapsulation technology favored decreased mobility of cadmium, copper, chromium, lead, nickel, and arsenic metals in acid tar. A drop in concentration of over 95% was obtained for the whole group of tracked metals. Thus, the results of the leaching test show that the level of metal concentrations is much lower than the pollution limits stipulated by international standards (ISO et al.) and Romanian Standards Order 95/2005.
- As a general finding, also noted in the published literature, the leaching of some heavy metals largely depends on the pH of the liquid (Ex. Pb and Cr).

Pb (lead) varies between 0.0003 and 0.0056 mg/kg in all stabilized samples.

It should be noted that the pH of the samples from which the metals are determined varies from 8.7 (at a **Pb (lead)** content of 0.008) to 10.0 (at a sulfur content of 0.002 mg/kg **Pb (lead)**).

It can be seen that a high pH affects the precipitation of **Pb (lead)**.

The concentration of **Pb (lead)** in the eluate will decrease with increasing pH due to the cement in the mixture used for stabilization/encapsulation.

Unfortunately, it was found that **Pb (lead)** is difficult to detect in the eluate when the pH is between 9 and 11 due to the formation of insoluble hydroxide. However, it can be detected at pH 12 due to the formation of an amphoteric hydroxide complex.

Cadmium- Cd concentrations in the eluate samples varied between 0.0001 and 0.0050 mg/kg.

Most eluate samples (approx. 87%) are contaminated with less than 0.002 mg/kg **Cadmium- Cd**.

The studied acid tar samples subjected to leaching contain a significant content of **Cadmium- Cd** with an average of about 30 mg/kg.

Cadmium- Cd leaching for all samples shows that the values of the concentrations of this metal were quite scattered, with values below 0.001 mg/kg for the first nine samples, a maximum in the case of sample 10 (0.005 mg/kg) and values below 0.002 mg/kg for the samples 12-39.

Also, cadmium hydroxide has a low solubility at pH 10 in a short solidification time.

As mentioned in the literature, cement is beneficial for **Cadmium-Cd** immobilization in all conditions.

A decrease in **Cadmium- Cd** migration with increasing pH is probably attributed to **Cadmium-Cd** commonly existing as hydroxide on cementitious materials; therefore, higher pH conditions accelerated the formation of the insoluble Cd(OH)2 precipitate.

A variation of the **Copper (Cu)** is detected in a concentration from 0.00083 and 0.0161 mg/kg,

The leachate's copper (Cu) concentrations are approximately 85% lower than 0.008 mg/kg.

Although it was found in the literature that the pH value does not influence

In copper (Cu) elution, which, when leaching the same sample, would have a general behavior like **Chromium (Cr)**, the values of **Chromium (Cr)** concentrations are about five times higher. An explanation of the lower concentrations of **Copper (Cu)** in the leachate resulting from the acid tar treated by encapsulation/stabilization would be the application of some recipes in which the agglomeration agent, sodium metasilicate, $Na_2SiO_3.9H_2O$, was added in larger quantities.

Chromium (Cr). Chromium, known as one of the most toxic metals, **Chromium (Cr)** measured in the eluate collected after acid tar treatment varies between 0.0010 and 0.084 mg/kg.

As in the case of copper, very high values of **Chromium (Cr)** concentrations are found (over 330 mg/kg), and none of the three recipes could achieve the appropriate reduction of **Chromium (Cr)** in the eluate.

Although **Chromium (Cr)** concentrations in the range of 30 to 100 mg/kg can be found in ordinary Portland cement, concentrations that can be added to those found in acid tar, the application of the three recipes formulated and applied in the treatment of acid tar led to values below 0.1 mg/kg chromium in leachate.

A noticeable trend for all samples can be observed when the cement content increases the **Chromium (Cr)** concentration.

This is due to the cement containing Cr_6^+, as the literature mentions.

At the same time, the additional presence of Cr_6^+ increased the cement's initial and final setting times.

It was concluded that the immobilization of Cr_6^+ by the cement-based encapsulation/stabilization technology was achieved due to the formation of a complex calcium chromate ($CaCrO_4$) with low solubility.

The cement hydration process was affected in the presence of Cr_6^+ because part of the Ca_2^+ in the cement reacted with CrO_4^{2-}.

Nickel (Ni) concentrations in the eluate varied between 0.0015 and 0.091 mg/kg dry substances.

It is found that the hydroxides of **Nickel (Ni)** and **Cadmium (Cd)** are incorporated in the hydrated cement matrices, which gives a good immobilization capacity for **Nickel (Ni)**.

Arsenic (As). It is distributed over a wide range of values in the untreated tar (between 1.4 and 589 mg/kg dry substances) and in the eluate (below 0.001 to 0.402 mg/kg).

The sample with 2 % cement gave a higher Arsenic concentration (As) than 0 % and 4 % cement.

For 4 % cement with different rubber chip content, the concentration of **arsenic (As)** also increases significantly.

This could be the leaching of As upon the formation of Ca-As precipitates.

Therefore, Ca-As precipitation increases with Ca in the cement.

Increasing the pH of the leachate, on the one hand, and the addition of CaO, on the other hand, favors it better.

As fixation when the leaching takes place in an alkaline environment.

Also, high As concentrations were in samples 21 and 24, in which the TPH content in the acid tar was high. Cyanides.

To determine the content of **free cyanides** in the eluted water, a UV-VIS Spectrophotometer DR 3900 was used to detect cyanides with concentrations between 0.01 mg/l and 0.6 mg/l.

Cyan concentrations between 0.013-0.368 mg/kg s.u. in the untreated acid tar reached concentrations < 0.001 below the detection limit in the leachate.

Chlorides, Sulfates, DOC (Dissolved Organic Compounds). Related to the content of chlorides, sulfates, and DOC, determined in the leachate, there is a reduction in the concentration of these substances with maximum values at sampling point 20, at a depth of 30 cm for DOC, respectively sulfates (2047, respectively 619 mg/kg).

The DOC content was between 108 and 2047 (with three values above 1000 mg/kg).

According to this research, the macro-scale application of the process for the stabilization and encapsulation of acid tar with TPH values below 200,000 mg/kg would allow the metal content from the group considered Pb+Cd+Cu+Cr+As to decrease below the imposed limits and DOC below 1000 mg/kg s.u.

The technological flow of the model is based on the following technological phases: supply of the material to be treated, dosing of treatment agents, aeration, homogenization, heating and maintaining a constant treatment temperature, controlling the technological parameters during the treatment process, and extracting the treated product.

In perspective, it is aimed to fulfill the objectives of future research:

- Add to evaluations based on leaching and chemical analysis the use of all microscopic analyses in studies of the long-term performance of stabilization/encapsulation technologies in the treatment of acid tars in the petroleum industry
- Classic extraction techniques (e.g., Soxhlet), already applied, to be completed and compared with new techniques (e.g., extraction with ultrasound, microwaves), thus capitalizing on the expected advantages related to the reduction of treatment times, extraction, the number of additives, the use of some waste as additives.
- The complex research which, in addition to the analyses focused until now, mainly on the inorganic components of the tar, should also add an organic analysis of the leachates, under the conditions in which the leaching tests would have a more realistic character, being carried out on batches with conditions adjusted (stirring time, water-solid ratio, temperature)
- For the statistical processing part, the analysis of several candidate mathematical models will be sought, as well as the evaluation function, and the mathematical model with the minimum value of the absolute average error will be chosen.
- Additional design and implementation of weathering tests of a different nature to foreshadow how acid tar transforms under different conditions, raising the possibility that a particular damaged form may become part of a potential remedial solution.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

- Mihaela Tita, and Daniel Tita carried out the concept of acid tar capsulation.
- Ion Onutu, Timur Chis analysis of this project and experimental research procedures analysis.
- Timur Chis and Lucian Ion Tarnu were responsible for the Statistics.

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Conflict of Interest

The authors have no conflicts of interest to declare.

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