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STABILIZATION OF ACID TARS PRESENT IN OIL RESIDUE LAGOONS

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Having been active for over 100 years, Romanian refineries have also produced large amounts of waste resulting from the complex processing of crude oils, most of which is stored in tanks to be processed later. The closure of 9 refineries (out of the existing 13) has also led to the abandonment of this waste treatment. After joining the European Union, Romania eliminated these acid tar lagoons and returned the decontaminated land to the local communities. However, eliminating these chemical substances (from acid tars and other waste to oil and petroleum products and chemical substances) is challenging, both because of their multiple physicochemical compositions and mainly given the lack of techniques that reduce ecological destruction (incineration or slow pyrolysis creates other pollutants). Acid tars are present in the waste of the crude oil processing industry and originate from the refining of some petroleum fractions (oil, paraffin). This article analyzes acid tars and proposes several solutions for their stabilization and encapsulation. The effects of their encapsulation on the primary pollutants present in acidic waste are also presented.

Keywords: refinery waste, acid tars, encapsulation, stabilization

1. Introduction

In terms of refinery, the quantities of solid residual materials resulting from the manufacture of finished petroleum products are within the limits of 3 - 5 kg/ton of crude oil processed. Over 80% of these residues are highly polluting due to the presence of organic toxins and heavy metals [1].

At present, it should be noted that the rational and complex processing of crude oil and its fractions no longer leads to waste production. The losses are minimal and technologically planned, moreover, all the resulting by-products are exploited [2].

Unfortunately, crude oil refining in Romania before the 1990s was carried out in simple refineries and without hydrorefining processes, leading to large amounts of residual waste such as acid tars, petroleum sludges, sludges containing petroleum products and infested soil, all of which are legally classified as hazardous waste [2] over 861 potentially contaminated sites due to petroleum operations (drilling, extraction, transport, processing) [3].

In refineries worldwide, this residual waste is processed by the following technologies:

- neutralization by applying calcium oxide directly (producing another pollutant);
- incineration in specialized equipment, releasing gases containing particulate contaminants;
- thermal decomposition occurs at temperatures between 260 and 650 ºC, producing free sulfuric acid and particulate pollutants;
- recovery of sulfonic acids neutralized by calcium oxide to create compounds used to build communal roads;
- neutralization of various agents;
- pyrolysis at high temperatures from 800–1200 ºC and decomposition at low temperatures from 150–350 ºC followed by the production of bitumen.

This study aims to identify a technology for encapsulating strong acids to be transported and stored under specific environmental conditions in line with legislation and used in the construction materials industry for communal and minor roads.

2. Strategy for analyzing and resolving acid tar issues

In addition to restructuring, the oil refining industry also faces environmental requirements and restrictive legislation regarding the quality of petroleum products. At present, refineries must comply with the following objectives [4]-[6]:

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1) the processing of crude oils with a high content of sulfur and metals, which are increasingly present in the depleted deposits in Romania;
2) alignment with the European requirements regarding the continuous improvement of the quality of gasoline and diesel, especially in terms of the drastic reduction in their sulfur content;
3) the need to reduce greenhouse gas emissions and waste from refining;
4) growth in the market of electric and hybrid machines as well as other equipment has decreased the demand for petroleum products.

This is precisely why only a small quantity of acid tars are produced from refineries and processed. Nevertheless, waste lagoons at closed refineries must be treated and eliminated quickly.

Acid tars are obtained from treating refined products with sulfuric acid during their synthesis. They are residual materials from the technologies applied from the foundation of the petroleum industry. Acid tar appeared at the end of the 19th century as a waste material due to the use of concentrated sulfuric acid to process distillate, motor and other petroleum oils [7]. Therefore, unsaturated and aromatic hydrocarbons, sulfur and nitrogen compounds as well as resinous substances, which affected the stability and performance of commercial petroleum oils, were removed by this process. Acid tars also result from the refinery of special oils such as those used in alternating current transformers in addition to hydraulic, medicinal and cosmetic oils as well as from the production of flotation reagents on top of the individual sulfonation of some hydrocarbons and petroleum fractions [8]. Meanwhile, acid tars are also generated during the alkylation of isobutene with olefins, a technological process necessary to manufacture octane components and stabilize aromatic compounds [9].

Acid tars are analytically characterized by how much free sulfuric acid they contain, their total organic matter and their consistency (viscosity) at the end of the process.

The presence of acid tars in Romania was confirmed as a result of the use of acids in the following industrial processes:

a) alkylation of gasoline and the manufacture of detergents
   Acid tars are easily handled liquids that are extremely stable over time;
b) oil refining
   These wastes are viscous, unstable and become more difficult to pump as they age. Interestingly, appreciable differences are found between acid tars obtained from paraffinic oils and those from naphthenic oils.

The process leading to the generation of acid tar results in an emulsion in which the upper layer contains the acid oil and the lower the acid sludge. The sludge contains products from secondary reactions, namely an excess of sulfuric acid and a small amount of oil/petroleum adsorbed on various solid particles.

Acid tars exhibit the following physicochemical behavior over time:

a) In the production phase, acid tars are obtained in an emulsified form, which is much less stable.
b) Over time, an upper phase is separated by a lighter emulsion. The continuous phase is the petroleum product and the dispersed phase consists of sulfuric acid and water. A thin film composed of sulfonic acids lies between the two phases.
c) The lower phase of acid tars consists of sulfuric acid, water as well as low-molecular-weight sulfonates and sulfates of nitrogen compounds. This phase appears as a cloudy, gray-black solution.
d) During their storage in pits, water from precipitation enters the upper layer, diluting the existing sulfuric acid. Meanwhile, the organic mass begins to oxidize (due to the uptake of oxygen from the atmosphere and the heating of the tar as a result of the adsorption of solar energy) and the temperature of this waste reaches 80-95 ºC.
e) During its oxidation, resinous, asphaltogenic and carcinoid compounds are produced, moreover, the tar matures and becomes a solid mass. The tar releases products into the atmosphere, mainly sulfur oxides, hydrogen sulfide, ammonia, carbonyl sulfide and water vapor.
f) After a long period of storage, acid tars age, forming a layer of organic mass similar to bitumen on their surface.

The mineral acidity of this layer referred to in f) is relatively low and contains compounds such as heavy sulfonic acids, heavy naphthenic-aromatic acids, metals and resins, asphaltenes, carbides and carbenes formed by polycondensation and polymerization. This layer usually does not contain free hydrocarbons or only trace amounts.

The lower layer of aged tars contains acidified water with dissolved compounds such as metal sulfates and sulfides of essential compounds from petroleum products [10],[11].

The transformation of acid tars over time leads to the formation of highly dense and viscous waste. Furthermore, over time, acid tars absorb oxygen and other strongly polar components which produce polymerization and polycondensation reactions with the appearance of macromolecular compounds such as resins and asphaltenes. Therefore, the tars resemble bitumen that solidifies at the interface with the environment.

The processing and/or elimination of acid tars is always topical, moreover, countries with highly developed industries and clear legislation have almost completely solved this problem.

3. Scope of this study and procedures

The analyses were carried out on stratified and surface samples, 40 in total, collected from 4 storage tanks of acid tars (*Table 1*), originating from the treatment of gasoline (tar 1), lamp oil (tar 2), lubricating oils (tar 3)

Table 1: Acid tar of Romanian refinery lagoons [5],[6]

Characteristics	Acid tar 1	Acid tar 2	Acid tar 3	Acid tar 4
Density, kg/m^3	1.62±0.1	1.43±0.1	1.33±0.1	1.27±0.1
Total acidity, % of mass	55.4±0.1	45.8±0.1	42.8±0.1	18.3±0.1
Sulfuric acid, % mass	46.3±0.1	33.2±0.1	39.7±0.1	17.5±0.1
Water content, % mass	3.30±0.1	5.6±0.1	7.6±0.1	3.8±0.1

and viscous lubricating oils (tar 4).The results confirm the presence of free sulfuric acid.

The analyses carried out on the samples collected from the acid waste storage basins showed that these treatments were helpful with regard to the finished products but presented a real danger to the environment with the highest concentration of residual acid originating from the treatment of gasoline and the lowest from the treatment of oils (which confirms the data from the specialized literature).

In Romania, the processing of waste such as acid tars was significantly reduced due to a lack of interest at the time of storage, namely the remediation of the generally extensive and heavily contaminated sites where the acid tars were stored was carried out by excavating, transporting and storing this waste in concrete pits that were often ineffectively covered.

The research on waste lagoons in Romania confirms the impossibility of treating acid tars by classical methods due to their aging, namely incineration, thermal decomposition or neutralization, which are highly expensive and uneconomical techniques. The only effective method is encapsulation followed by the neutralization of acid waste. To create new technologies for encapsulating and treating acid tars, a field study was carried out over 3 years by investigating several acid tar waste storage lagoons related to closed and abandoned Romanian refineries. From the 30 oil waste storage lagoons, 300 samples containing acid tar were taken. The samples were collected as follows:

a) Each lagoon was mapped, filmed and photographed by drone inspection.
b) Having been mapped, the areas that had been depolluted or excavated (which were decontaminated according to the documents drawn up by the environmental authority) were delimited.
c) The polluted areas were delimited with the help of grids with 4 sampling sites from the interface between the pollutant and soil or the protected lagoon and 6 randomly chosen ones depending on the size of the lagoon.
d) Each sample was collected by drilling and taking cores of the soil-pollutant-acid tar up to 2 m deep to analyze the vertical composition and separation processes of acid tars rather than the amount of pollutant.
e) All 300 samples were grouped according to the origin of the acid tar, namely from the treatment of gasoline, diesel and light or heavy lubricating oils. They were easily divided because the storage lagoons were located in the treatment areas of the refined products, that is, gasoline, diesel as well as light and heavy lubricating oils, rather than in areas especially designed for storage.
f) All the samples taken were dried with water and evaporated gases analyzed separately.
g) Afterwards, the samples were crushed and analyzed according to the protocol created for this purpose, determining the main physicochemical properties, the level of contamination in terms of their depth and the average amounts of the analyzed contaminants in particular.
h) For each sample analyzed and subsequently for each group of samples as well as each depth interval of pollution, the extreme values, standard deviation and values that do not statistically correctly identify the level of contamination were determined in terms of pollution and its evolution over time.

The harvesting method used complies with Romanian law according to the procedures and technical norms regarding the identification of damage caused to the environment to determine the level of responsibility for their remediation. It is based on the provisions of Articles 36, 42 and 48 of Environmental Protection Law no. 137/1995 as well as the provisions of Article 15 paragraph (5) from Water Law no. 107/1996 [3].

The experimental data was statistically processed using artificial intelligence (Data Science) to ensure a good prediction regarding the properties of the acid tars from the waste lagoons and the associated leachate. The collected and statistically processed data only eliminated outliers and was handled without plotting a graph of the evolution of acid waste behavior over time.

Given that the laboratory study analyzed the quality and physicochemical properties of some deposits totaling 80,000 m^3 of waste (acid tars, oil residues and acid water) originating from a refinery that ceased to operate in the year 2000, the collected samples were defined as stabilized waste (acid tar). The physicochemical analysis of the acid tar samples is shown in *Table 2*. This study presents only the characteristics necessary to create an additive for the encapsulation/neutralization of this waste. Analytical determinations of the collected samples were carried out according to the internationally used standardized methods.

To establish a new encapsulation technique, the following research program was agreed [12],[13]:

a) sampling of acid tar samples from a bottle and their characterization according to the following indicators: pH, total hydrocarbons as well as metal, cyanide, chloride and sulfates content;
b) characterization and determination of indicators from the stabilized acid tar leachate: pH; total hydrocarbons; metal, cyanide, chloride and sulfate content; TDS (Total Dissolved Solids); TOC (Total Organic Carbon) and DOC (Dissolved Organic Carbon);
c) identifying, testing and establishing the optimal conditions for stabilizing acid tar;

Table 2: Stabilized acid tar

Characteristics	Average	Experimental results
Organic products, % mass	40 - 60	58.0
Inorganic products, % mass	20 - 60	27.0
Calorific value, kcal/kg	4 900 - 5 300	4850
Water, % mass	15 - 20	14
Acidity, mg KOH/g	10 - 100	38.0
Sulphur, % mass	0.5 - 3	2.0
Fe, % mass	0.008 - 0.4	0.2
Ca, % mass	0.1 - 0.3	0.26
Mg, ppm	38 - 925	400.0
Mn, ppm	3.7 - 15	11.0
Ni, ppm	4.0 - 85	48.0
Zn, ppm	35 - 157	123
Pb, ppm	13 - 237	88.0
Cu, ppm	2 - 11.4	8.8
Hydrocarbons, % mass	15 - 20	17.2
Resins, % mass	35 - 50	37.4
Asphaltene, % mass	15 - 20	17.3

d) characterization of the stabilized acid tar leachate and compliance with the legal provisions;
e) capitalizing on laboratory research in the treatment of acid tars by proposing alternative technical solutions applied on a macroscale for the treatment of acid tars in situ and to reduce the impact of acid tars on environmental factors;
f) estimating the costs per ton of treated waste, the materials used and the specific levels of consumption associated with the treatment.

The treatment technology of acid tar-type waste refers to a composition and a process necessary to achieve in situ physical and chemical stabilization. Treating soils contaminated with acid tar needs neutralization, stabilization and encapsulation processes. The encapsulation/neutralization additive recipes and the encapsulation/neutralization process are particularly applied to acid tar with a total hydrocarbon content below 200,000 mg/kg and DOC value below 1000 mg/kg in particular whose composition is not uniform.

The pH, Total Petroleum Hydrocarbons (TPH), heavy metals, TOC, DOC and sulfate content can vary per meter both in terms of length and depth. Since no gas emissions were detected during the collection of the acid tars subjected to analysis and treatment, these aspects were neglected. This is explained by "historical" acid tars in Batal from over 20 years ago.

Worldwide, several technologies have been developed for the treatment of acid waste that results from refining petroleum products. When treated 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, an emulsifier, strengthening additives, absorbents and sodium metasilicate (*Table 3*). The remaining mass is represented by acid tar subjected to stabilization.

Table 3: The composition required for the neutralization, stabilization and encapsulation of acid tar

Compound	(%)
Cement	3-20
Sand	2-5
Lime	3-8
Sodium hydroxide	1-10
Bentonite	1.0-2.8
Emulsifier	1-2
Strengthening additives	1

Identifying the potentially applicable reagent depends on several factors, including the contaminant to be treated, the concentration of pollutants in the acid tar, the geotechnical and acid tar properties, required performance parameters as well as minimum acceptable performance criteria for the treated acid tar. The identification and selection of the reagents applied in the experiment was based, on the one hand, on the technical literature consulted in the theoretical research and, on the other hand, on the experience of the author in implementing stabilization/encapsulation projects. Therefore, several candidate reagents were 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 in the chemical behavior of the metals in the acid tar, but also took into account the cost and history of the process. In the present case, the performance of the technology was measured and composition for the treatment of waste analyzed from bottles, while the stabilization/solidification in situ was investigated through several encapsulation formulae of acid waste.

As a result, in the first stage to encapsulate acid tars, the following mixture was used measured in mass % relative to acid tar:

a) Cement without additives: 25%,
b) Bentonite: 2.5% (by weight),
c) Acid tar: 36% (by weight),
d) Loam soil: 18% (by weight),
e) Clay: 18% (by weight).

The solidification/stabilization treatment applied to the acid tar under these conditions exhibited the following disadvantages:

a) The pH of the eluate after mixing acid tar with bentonite, loam soil and clay 1/10 L/S was between 2 and 3 (acidic environment).
b) The dissolved components were not chemically bound.

Table 4: Mixtures for encapsulating acid tar

Compound	Mixture 1	Mixture 2	Mixture 3
Sodium metasilicate, %	0.30	0.50	0.80
Emulsifier	1.00	3.50	4.00
Calcium oxide	8.00	3.00	7.00
Magnesium oxide	0.10	0.20	0.30
Bentonite	1.00	2.00	2.80
Sand	2.00	5.00	3.00
Cement	3.00	5.00	8.00
Reinforcing additives	1.00	1.00	1.00
Absorbent (oil absorbent)	1.00	1.00	1.00
Sodium hydroxide	1.00	1.00	1.00

c) The contaminant particles were not encapsulated in an impermeable cover.
d) The hazardous components were not chemically fixed by reducing their solubility.
e) The toxicity of the contaminants was not reduced.

Later, 3 mixtures were established for treating acid tars according to *Table 4*. Mixture 1 was applied for acid tars with high pH and low TPH values. Mixture 3 was used for acid tars with low pH and high TPH values. For tars with medium TPH values, Mixture 2 yielded the best results. It was found that TPH and pH values amongst other indicators, including the concentrations of various metals in the initial acid tar, influence the efficiency of the mixture used.

If the application of the chosen mixture did not decrease the concentrations below the limits stipulated in Law no. 95/2005, the application of the other 2 mixtures was applied. All these attempts were completed by filing 2 patents, one international and the other national. After applying the mixtures accordingly, a significant decrease in the parameters and compliance with the regulations stipulated in Law no. 95/2005 was observed.

The following chemical compounds were used in the mixtures:

Sodium metasilicate

Sodium metasilicate was added comprising 0.3 to 0.8 % mass. As argued in the literature, the final performance of the stabilization/encapsulation technology applied is determined by the quality and intrinsic properties of the additives as well as binders in the mixtures.

The added sodium metasilicate exhibits 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 enhance the mixtures because it maintains the cleaning efficiency of the added emulsifier and absorbent mainly by reducing water hardness. It has also been reported that Cu can bind to cement using this agglomerating agent, that is, sodium metasilicate, Na_2SiO_3 x $9H_2O$.

Ordinary Portland Cement

Ordinary Portland Cement (OPC) used in the present study facilitates the immobilization of Cr, Cu, Zn, Mn and Pb. The addition of cement increases the degree of immobilization and the curing time of the hardened material. This reference is attributed to the pozzolanic and/or hydraulic properties of the cement on the microstructure of the hardened material. Additives added to the cement and the hydration reactions in the mixtures favor the formation of the specific microstructure, facilitating the immobilization of dangerous elements.

Sand

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

Calcium oxide

Calcium oxide (slaked lime, quicklime), presented as a white powder, is used to neutralize the acid tar. In addition to the neutralizing effect, the calcium oxide and emulsifier contributed to the transition of the metals from a volatile to stable phase. The added lime favors immobilization, especially of Cd, Cu, Ni, Pb and Zn.

Sodium hydroxide

Sodium hydroxide neutralizes the tar acid tar and the reaction is strongly exothermic.

Emulsifier

The emulsifier stabilizes the pH and results in a homogeneous mixture of the stabilized acid tar. The presence of the emulsifier leads to a higher degree of encapsulation of the acid tar by breaking the hydrocarbon chains and embedding the compounds faster and deeper. The emulsifier is used quickly to mix and incorporate all the compounds proposed in the mixtures elaborated on in the thesis according to the Certificate no. 107443 granted by the State Office for Inventions and Trademarks [12],[13].

Bentonite and cement

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

Absorbent

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

The freshly prepared sample of acid tar is homogenized and binders added to stabilize as well as encapsulate the acid tar. Following treatment in the laboratory, the stabilized acid tar is presented as a compacted block. The values of the pollutants identified in its leachate are below the limits permitted according to Law no. 95/2005.

Table 5: Acid tar concentration

Indicators	Value minimum	Value mean	Value maximum
pH	0.20	3.90	5.20
TPH in soil, mg/kg dry substances	48,333	477,062	200,000
Pb, mg/kg	42	400	478
Cd,mg/kg	1	5	126
Cu, mg/kg	2.6	100	789
Cr, mg/kg	3	70	452
Ni, mg/kg	2	40	859
As, mg/kg	1.4	25	589

4. Results

Final processing and verification found that a stabilized and encapsulated material with low degrees of permeability and leachability as well as moderate to high resistance was obtained, meeting all the performance criteria.

The volume of the treated acid tar increased by up to 5% of the initial volume of the acid tar before treatment. This aspect is essential in the following 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 the need to dig additional pits to store the surplus resulting from the treatment.

Since acid tar is a particular waste, its treatment by stabilization/encapsulation had to be carried out carefully as elaborated on in the literature review. Firstly, being unstable from a geotechnical point of view, it can exhibit creep effects depending on the type and temperature. Secondly, leachates of organic compounds (hydrocarbons) and inorganic compounds (sulfuric acid, metals) can be recorded in the water. After adding and mixing the additives, no significant heating of the neutralized and treated acid tar was observed, leading to the volatilization of specific contaminants. Furthermore, no sulfur dioxide emissions were detected since an "old" acid tar was treated.

Since the treated and stabilized acid tar was not exploited as a construction material, it was not analyzed from a geomechanical point of view in the thesis. Once immobilized in the matrix, contaminants 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, acid tar samples from the field under study were taken, their composition determined and the following indicators measured: pH; TPH; metal, cyanide, chloride and sulfate content as well as DOC were compared with the limits stipulated by Law no. 95/2005. At all locations, the depth from which acid tar samples were taken was approximately 5-30 % of their weight.

5. Discussion

Analysis of the experimental data led to the following conclusions as presented in *Table 5* [14].

The strongly acidic character intensified the categories of potential waste stored in the studied area (sludge, oil sludge) due to the mixture of these wastes with the acid tar. The highest TPH concentration was detected in all acid tar samples but decreased approximately fourfold at a depth of 30 cm. The study of TPH concentrations whereby large-scale cement-based stabilization/encapsulation technologies were applied to inorganic waste, including metals, is essential under the conditions reported when organic substances can be easily leached.

Unfortunately, little information is available on organic leaching from acid tars after applying stabilization/encapsulation technologies or on the effects of organic compounds on complex reactions, which can alter the 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.

The concentrations of the analyzed metals were determined according to the Analysis Method SR EN ISO 15586:2004: Determination of trace elements by atomic absorption spectroscopy with a graphite furnace and the method for the rapid detection of trace elements. An atomic absorption spectrometer with a graphite furnace and a Mobile EDXRF Device with X-ray detection were used to rapidly detect trace elements. 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 waste stored in polluted areas and in the additives used in the refining processes, the absorption of metals from the storage tanks and the supply, as well as the natural presence of metals in the parent rock from which the crude oil was extracted and even the materials with which the stabilization/encapsulation is carried out, e.g. cement.

As a general finding, the values determined and recorded for the concentrations of the metals Pb, Cd, Cu, Cr and As are noted. However, their values in the initial acid tar exceeded the maximum allowed limits. However, in the leachate stabilized for 1 day, low values were recorded, some even below the limit of quantification of the determination methods.

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

5.1. pH

The eluates were analyzed to determine the acidity according to SR EN ISO 10523:2012 Determination of pH. In general, it was found that increasing the pH from between 0.2 and 5.28 (untreated acid tar) to 8.7 and 10 (in the case of the leachate) was beneficial in increasing

the leaching performance, e.g. in the speciation of metal contaminants.

5.2. TPH

The TPH content of the leachate was determined using the Method SR EN ISO 9377-2:2002 — determination of the Hydrocarbon Oil Index.

The stabilization-encapsulation technology applied in the study to treat acid tar confirmed that the organic materials—hydrocarbons—do not react with the inorganic binders from the 3 applied mixtures due to the significant differences in hydrophobicity and polarity between the organic contaminants and the organic binders. This may often lead to ineffective immobilization of hazardous organic hydrocarbon contaminants in the solid matrix and significant leaching of many pollutants.

However, the final results of the leaching tests showed a good degree of efficiency in reducing the TPH in the leachate.

5.3. Metals

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

The leachate was prepared and analyzed 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 OPC used in the present study contributed to the immobilization of Cr, Cu, Zn, Mn and Pb in particular. The addition of cement increases the degree of immobilization and 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 mixtures contributed to the transition of the metals from the volatile to a stable phase. The added lime favors immobilization, especially in 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. Meanwhile, 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 quickly stabilized, delaying the formation of the crystalline structure and resulting in a more amorphous material. Incorporating modified and natural clays or sodium silicate into the stabilizing mixture with the cement can reduce the interference of organic contaminants with cement hydration and improve stabilization.

The different elements in the formulated mixtures presented different leaching potentials correlated with the curing time, the compositions of the binders as well as the initial and final pH, suggesting that how each metal contaminant is preliminarily released should be considered for the practical immobilization of the contaminated materials.

The applied encapsulation technology decreased the mobility of cadmium, copper, chromium, lead, nickel and arsenic in the acid tar. The tracked metal group experienced a drop in concentration of over 95%. Therefore, the leaching test results show that the metal concentration 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, e.g. Pb and Cr.

Lead

Lead (Pb) concentrations varied between 0.0003 and 0.0056 mg/kg in all the stabilized samples. It should be noted that the pH of the samples from which the metal concentrations were determined varies from 8.7 at a Pb concentration of 0.008 mg/kg to 10.0 at a Pb concentration of 0.002 mg/kg.

It can be seen that a high pH affects the precipitation of Pb. The concentration of Pb 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

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 Cd.

The studied acid tar samples subjected to leaching contain a significant amount of Cd with an average of approximately 30 mg/kg.

Cd leaching in all samples showed that the concentrations of this metal varied considerably with values below 0.001 mg/kg for the first 9 samples, a maximum in the case of sample 10 (0.005 mg/kg) and values below 0.002 mg/kg for samples 11-39.

Furthermore, the solubility of cadmium hydroxide is low at pH 10 over a short solidification time. As mentioned in the literature, cement enhances the immobilization of Cd under all conditions. Since a reduction in Cd migration as the pH increases is probably attributed to Cd commonly existing as hydroxide on cementitious materials, higher pH conditions accelerated the formation of the insoluble $Cd(OH)_2$ precipitate.

Copper

The copper (Cu) concentration detected varied between 0.00083 and 0.01610 mg/kg. The leachate's Cu concentrations are approximately 85% lower than 0.008 mg/kg. However, it was found in the literature that the pH is not influenced.

In terms of Cu elution, which, when leaching the same sample, generally behaved like chromium, the Cr concentrations were approximately 5 times higher.

The lower Cu concentrations in the leachate resulting from the acid tar treated by encapsulation/stabilization can be explained by applying some mixtures in which the agglomeration agent, sodium metasilicate $Na_2SiO_3.9H_2O$, was added in larger quantities.

Chromium

Chromium (Cr) concentrations, known as one of the most toxic metals, measured in the eluate collected after acid tar treatment varied between 0.0010 and 0.0840 mg/kg.

As in the case of copper, very high values of Cr concentrations were found (over 330 mg/kg) and none of the 3 mixtures could achieve an acceptable reduction in the Cr concentration in the eluate. Although Cr concentrations between 30 and 100 mg/kg can be found in ordinary portland cement which can be added to those found in acid tar, the application of the 3 mixtures formulated and applied in the treatment of acid tar led to values below 0.1 mg/kg of chromium in the leachate.

A noticeable trend for all samples can be observed when the cement content increases the Cr concentration since cement contains Cr^{6+}, as mentioned in the literature. Meanwhile, the additional presence of Cr^{6+} increased the initial and final setting times of the cement. It was concluded that the immobilization of Cr^{6+} by the cement-based encapsulation/stabilization technology was achieved due to the formation of a calcium chromate complex ($CaCrO_4$) of low solubility. The cement hydration process was affected in the presence of Cr^{6+} because a proportion of the Ca^{2+} in the cement reacted with CrO_4^{2-}.

Nickel

Nickel (Ni) concentrations in the eluate varied between 0.0015 and 0.0910 mg/kg of dry substance.

The hydroxides of Ni and Cd are incorporated in the hydrated cement matrices, which gives Ni a good immobilization capacity.

Arsenic

Arsenic (As) concentrations varied considerably in the untreated acid tar (between 1.4 and 589 mg/kg of dry substance) and eluate (below 0.001 to 0.402 mg/kg).

The sample containing 2 % cement yielded a higher As concentration than when 0 and 4 % of cement were used. For 4 % cement with different amounts of rubber chippings, the As concentration also increased significantly, possibly because of the leaching of As upon the formation of Ca-As precipitates. Therefore, Ca-As precipitation increases with the Ca concentration in the cement.

Increasing the pH of the leachate, on the one hand, and adding CaO, on the other hand, is more favorable. Fixation occurs when the leaching takes place in an alkaline environment.

Furthermore, high As concentrations were recorded in samples 21 and 24 in which the TPH contents in the acid tar were high.

5.4. Cyanides

To determine the concentration of free cyanides in the eluted water, a UV-Vis DR3900 Spectrophotometer was used to detect cyanide concentrations between 0.01 and 0.60 mg/l. Cyanide concentrations between 0.013 and 0.368 mg/kg s.u. in the untreated acid tar reduced to <0.001 mg/kg in the leachate, which is below the detection limit.

5.5. Chlorides, Sulfates, DOC

The concentration of chlorides, sulfates and DOC in the leachate reduced with maximum values at sampling point 20 at a depth of 30 cm for DOC and sulfates of 2047 and 619 mg/kg, respectively. The DOC concentration was between 108 and 2047 mg/kg with 3 measurements above 1000 mg/kg.

According to this research, the macroscale application of the process for the stabilization and encapsulation of acid tar with TPH values below 200,000 mg/kg would allow the metal concentration from the group considered, that is, Pb, Cd, Cu, Cr and 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, as well as extracting the treated product.

6. Conclusions

Based on the literature, which was correlated with the practical results, a technology to treat the studied acid tar was sought. The untreated contaminated material was characterized and the performance of the technologies at different stages evaluated.

Solidification/stabilization technologies are usually used to treat soils and sludges containing heavy metals. The establishment of the rehabilitation technology and its feasibility were evaluated through an analytical study in the laboratory. The treatability tests carried out in the laboratory allowed for the technologies to be evaluated before their selection as well as the proposal of design parameters for the process and subsequent scaling up for implementation on a macroscale in the field.

An experimental procedure was applied that took into account representative parameters (type of waste/tar, its specifications, potential air emissions of VOCs, dust and odors, necessary materials and binders, etc.). Acid tar sampled from lagoons as well as the indicators - namely pH, TPH in addition to the concentrations of metals from

the Pb, Cd, Cu, Cr, Ni and As group, cyanides, chlorides, DOC and sulfates - were mixed and homogenized.

The formulation, preparation and testing of several mixtures for the treatment of acid tar samples taken from the waste lagoon sites highlighted the fact that the composition of the acid tar was not uniform and the values of the leading analyzed indicators were higher than the legal limits.

Several treatment mixtures were tested, of which three representative mixtures were finally retained. The curing process of the samples was analyzed as a function of time by visual examination. The testing process was stopped for mixtures that did not yield good results. By examining the distribution of additives in the final mixture as well as their mixing ratio in the 3 distinct mixtures, the following was noted:

- The concentrations of strengthening additives, absorbent and sodium hydroxide (approx. 1.00% each) were constant.
- Variable amounts of emulsifying agents produced by Eurototal (1.00, 3.50 and 4.00%, respectively) were used.
- increase in cement concentration (from 3.00% in Mixture 1 to 8.00% in Mixture 3);
  The cement concentration was increased from 3.00% in Mixture 1 to 8.00% in Mixture 3.
- The added calcium oxide concentration varied from 8.00% in the case of Mixture 1 to 7.00% in Mixture 3.
- The bentonite concentration increased from 1.00% in Mixture 1 to 2.80% in Mixture 3.
- A relatively constant increase is sodium metasilicate concentration was noted of 0.30, 0.50 and 0.80% for Mixtures 1-3, respectively.
- It was found that the TPH, pH and other indicators, including the concentrations of various metals, influence the effectiveness of the mixture. Therefore, if the application of the chosen mixture did not decrease the contaminant concentrations below the limits stipulated in Law no. 95/2005, one of the other two mixtures was used. If the second mixture did not yield the expected results, the third mixture was used.
- After completing the treatment in the laboratory, the stabilized acid tar was presented in the form of a compacted block and the values of the pollutants identified in its leachate were below the maximum values stipulated in Law no. 95/2005.
- The leaching capacity of the Pb, Cd, Cu, Cr, Ni and As group of metals from the stabilized and encapsulated material was evaluated because the encapsulation of acid tar reduces the mobility of the transported toxic substances. However, it cannot be guaranteed that the stabilized poisonous materials remain within the treated acid tar, especially after the acid tar has been damaged or come into contact with corrosive agents.

Although it is challenging to establish the effectiveness of the stabilization/encapsulation process applied to acid tar from waste lagoons, this can be evaluated by performing leaching tests in the laboratory.

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