CONTRIBUTIONS TO ASSESSMENT AND REMEDIATION OF ACID TARS LAGOONS

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ABSTRACT. Acid tars, a waste unique to the oil processing industry, pose a significant toxicity risk. These by-products originate from refining certain petroleum fractions, such as oil and paraffin, and are commonly found in the waste streams of crude oil processing. In Romania, particularly in the post-war period, acid tars were predominantly managed through storage. Although advancements in catalytic processes have considerably reduced the generation of acid tars in the Romanian refining industry, an efficient treatment method is still required to address the existing acid tars lagoons. The present research refers to a case study carried out on a laboratory scale for the physico-chemical stabilization/encapsulation of acid tars from a lagoon belonging to a refinery in Prahova-Romania county.

The experimental program aimed at formulating and applying optimal stabilization recipes for acid tar from the selected lagoon was conducted to reduce the total hydrocarbon and toxic metal content, in compliance with Order No. 95 of 12.02.2005 from Romanian legislation.The leaching data showed that the recipes that stabilize and encapsulate acid tar provide a good immobilization capacity for the five heavy metals (Pb, Cd, Cu, total Cr, Ni)

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and As, while their releases are dependent on the pH- and varies with the total hydrocarbon content of the treated tar. The laboratory study carried out and presented in this work, as well as the results obtained after performing the leaching test, allow the extrapolation and application of this stabilization - encapsulation procedure on a macro-in situ scale and the remediation of the lagoon where the acid tar was stored.

Keywords: refinery waste, acid tars, lagoon, encapsulation, stabilization, total petroleum hydrocarbons (TPH), heavy metals and As, leaching test.

INTRODUCTION

The oil industry as a whole generates waste from both extraction and refining operations, including drilling fluids, hydrocarbon- and salt-contaminated wastewater, sludge from oil effluent treatment plants, tank cleaning sludge, acid tars, spent catalysts, and bleaching earth. [1,2].

In Romania, in 2014, there were 861 potentially contaminated sites due to petroleum operations (drilling, extraction, transport, processing) [3].

In line with the European Commission's initiatives to remediate hydrocarbon-polluted environments, an area of 1,054,549 square meters was decontaminated, accounting for 84% of the total area recorded at the national level. [4,5].

Among the wastes specific to the oil processing industry, acid tars present a particular *toxicity hazard [6].* Acid tars were obtained in the late 1800s, by the treatment of refining products with sulfuric acid in synthesis processes [7].

Acid tars also result from the refining of specialty oils, including those used in alternating current transformers, hydraulic systems, medicinal and cosmetic applications, as well as from the production of flotation reagents and the sulfonation of specific hydrocarbons and petroleum fractions. [8, 9, 10, 11, 12].

Romania, like countries such as the USA, UK, the Netherlands, Belgium, Germany, Latvia, Slovenia, Slovakia, China, Zimbabwe, and Ukraine, also stores acid tar in the open air, in spent pits, storage ponds, lagoons, or near landfills. [3,5,6].

The research on the waste lagoons fields in Romania confirms the impossibility of treating acid tars by classical methods (due to their aging), incineration, thermal decomposition, or neutralization, which are techniques with high costs and low economic results [4,13].

In this paper, an experimental study was carried out regarding the selection, evaluation and application of a original variant of treating acid tars from a refinery lagoon in Prahova, Romania. The **stabilization/ encapsulation (S/E)** technology was chosen and applied, which does not destroy the tracked contaminants but keeps them from "leaching" at lower concentrations, safe for the environment [11]. Leaching occurs when water from rain or other sources dissolves and carries away contaminants. We achieved the validation of the process applied by S/E of acid tars by performing the leaching test, a useful method for assessing and evaluating the potential mobility of different contaminants in acid tars and soil.

RESULTS AND DISCUSSION

Results

Before applying an in situ remediation technology, it is necessary to know the degree of contamination of the lagoon that will be treated.

Therefore, in the present work it was necessary to provide a rapid but robust characterization of the acidity, the degree of hydrocarbons and heavy metals and As contamination in acid tar, so that appropriate treatment/ remediation techniques could then be used.

The characterization of fresh acid tar was conducted by determining key indicators such as pH, total petroleum hydrocarbons (TPH), heavy metals (Pb, Cd, Cu, total Cr, Ni), and As. For the treated tar, additional parameters such as sulfate content and dissolved organic compounds (DOC) were also measured.

The obtained experimental data were analyzed, evaluated and then validated. The samples taken and analyzed from the site of selected lagoon, belonging to a refinery in Romania, confirmed the inhomogeneous composition of the stored acid tar, the values of the main indicators considered and analyzed varying as follows (Figures 1-8):

- pH value between 0.20 and 5.28
- THP content between 48 333 and 477 062 mg/kg dry substance (d.s.)
- Metals content:
    - Lead between 42 and 2235 mg/kg d.s.
    - Cadmium content between 1 and 126 mg/kg d.s.
    - Copper between 2.6 and 789 mg/kg d.s.
    - Nickel between 2 and 859 mg/kg d.s.
    - Total chromium between 3 and 452 mg/kg d.s.
- Arsenic content: between 1.4 and 589 mg/kg d.s.
- Cyanides content between 0.013 and 0.380 mg/kg d.s.

- Chlorides content between 9.08 and 844 mg/kg d.s.
- Sulphate content between 54.01 and 618.9 mg/kg d.s.
  DOC between 108 and 2047 mg/kg d.s.
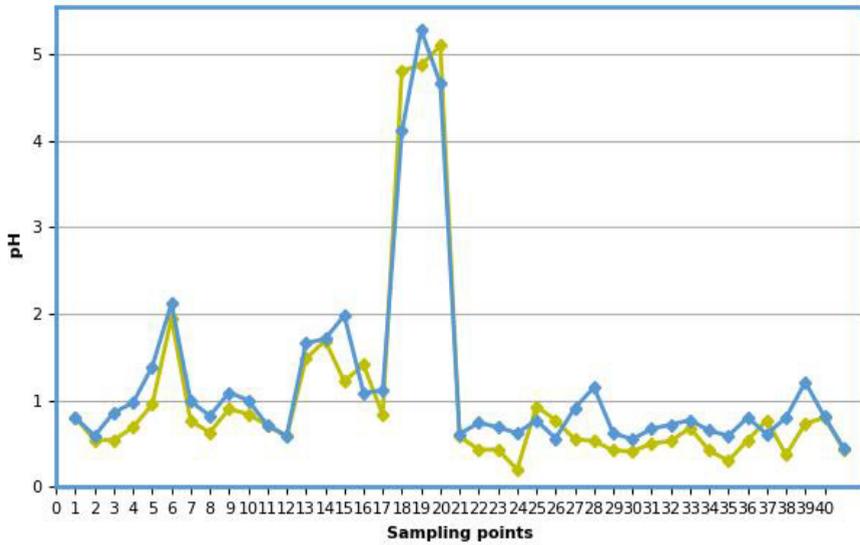
Figure 1. pH values of untreated acid tar samples.
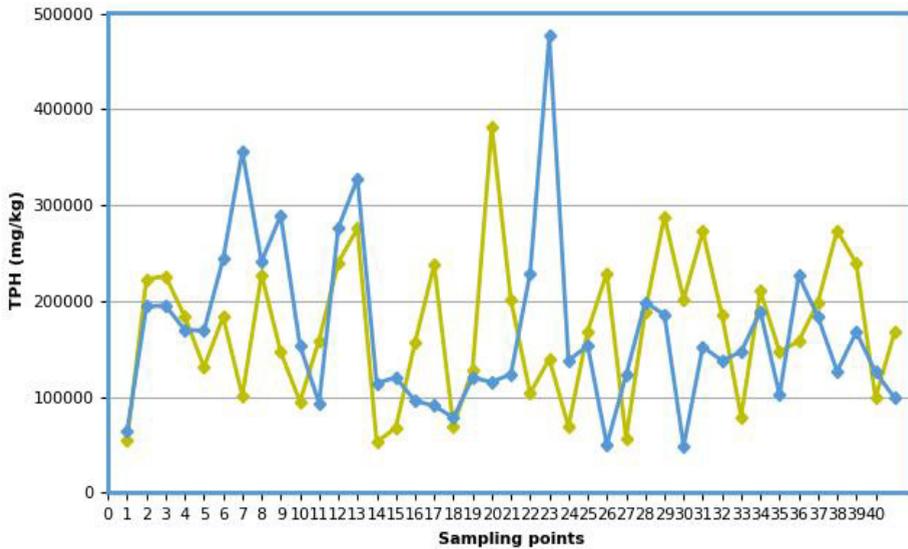
Figure 2. THP content of untreated acid tar samples.
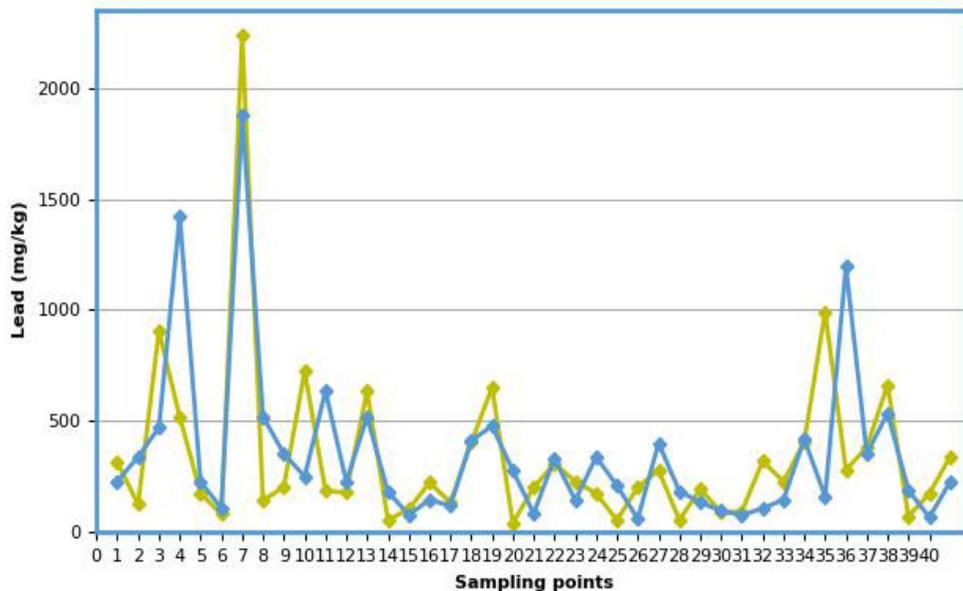
Figure 3. Lead content of untreated acid tar samples.
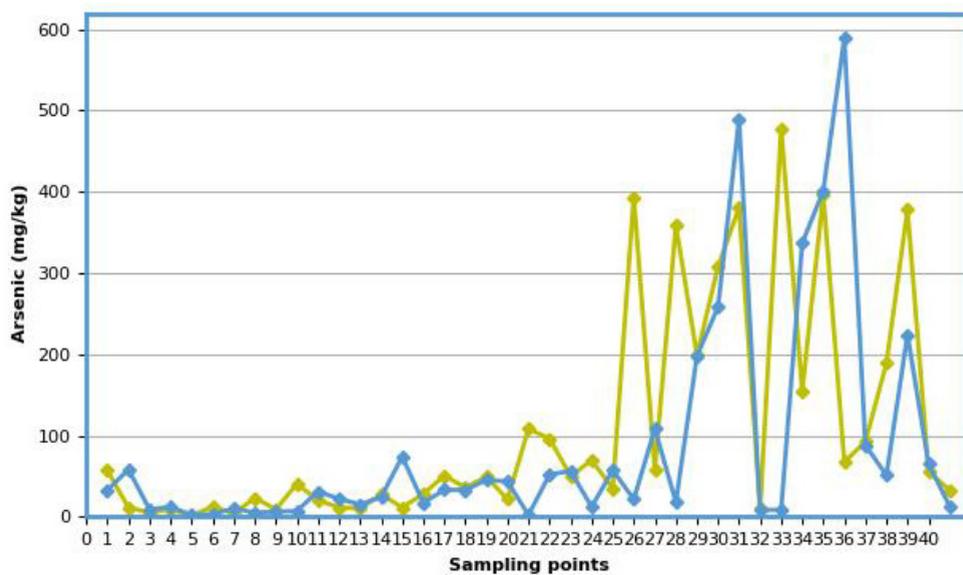
Figure 4. Cadmium content of untreated acid tar samples.
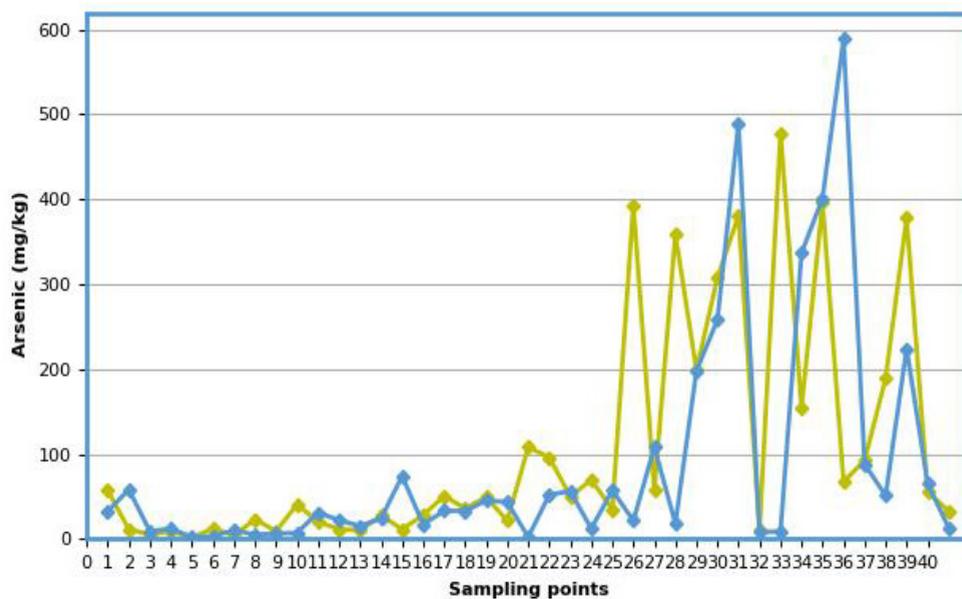
Figure 5. Copper content of untreated acid tar samples.
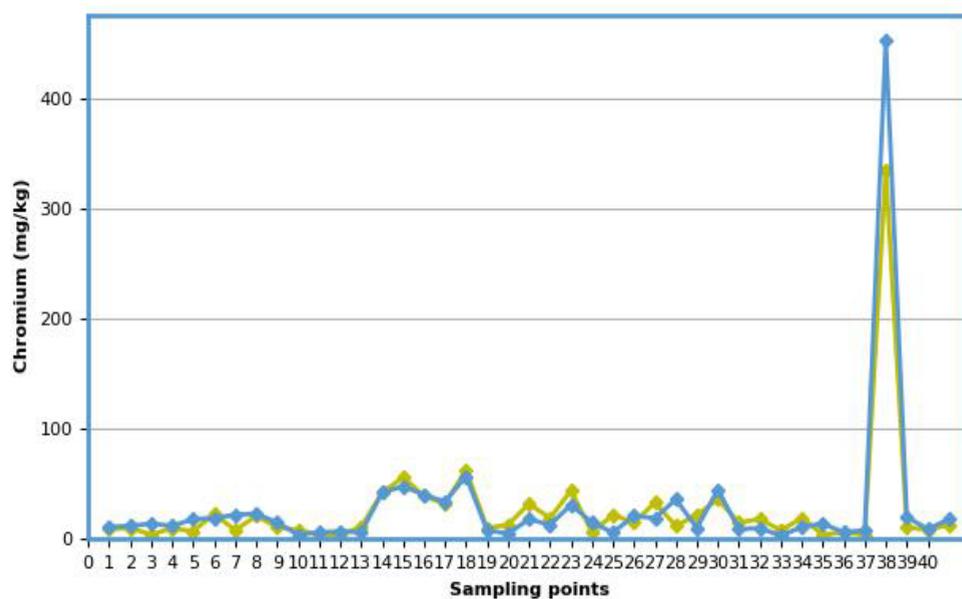
Figure 6. Chromium content of untreated acid tar samples.
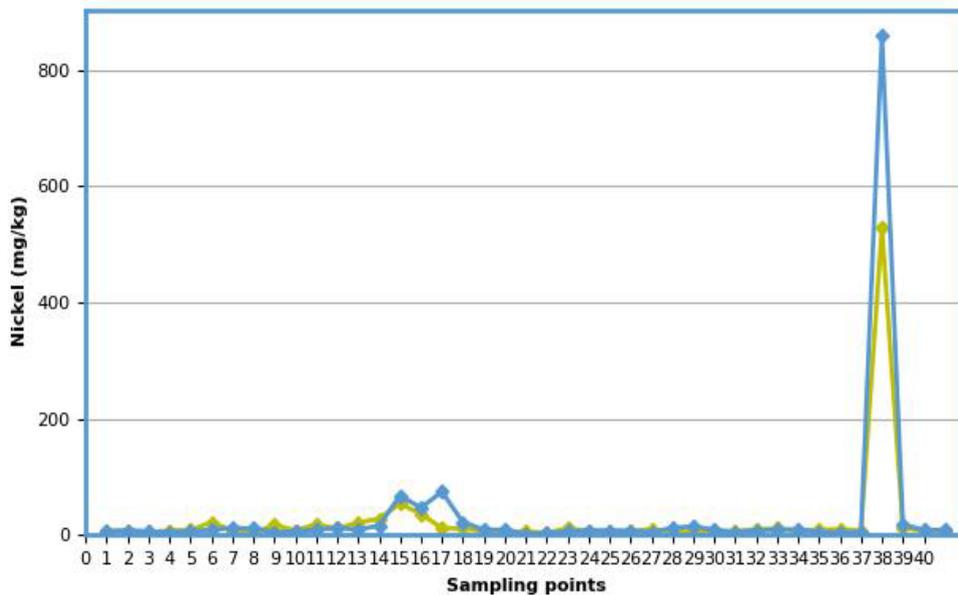
Figure 7. Nickel content of untreated acid tar samples.
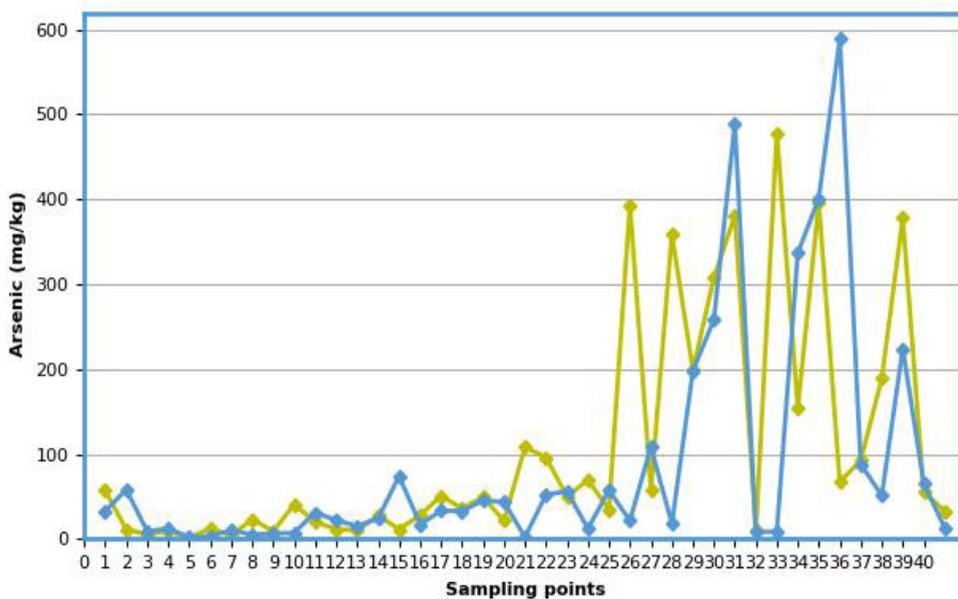
Figure 8. Arsenic content of untreated acid tar samples.

In the stabilization/encapsulation treatment applied to acid tars, the following substances were used as additives and filler materials: cement, sand, calcium oxide, sodium hydroxide, bentonite, emulsifiers, strengthening additives, absorbents, and sodium metasilicate (Table 1). The remainder, up to 100%, was composed of the acid tar undergoing stabilization.

The identification and selection of reagents used in the experiment were based on a review of technical literature from the theoretical research, as well as the author's experience in implementing stabilization and encapsulation projects.

Table 1. The composition for the neutralization, stabilization and encapsulation of acid tar

Ingredient	(%)
Cement	3-20%
Sand	2-5%
Calcium oxide	3-8%
Sodium hydroxide	1% - 10%
Bentonite	1-2,8%
Emulsifier	1-2%
Strengthening additives	1%

Finally, three recipes were established for treating acid tars, according to Table 2.

The first recipe was applied for tars with high pH values and low TPH values (acid pH value is 10.3).

The third recipe was used for tars with low pH values and high TPH values (acid pH value is 8.5).

For tars with medium TPH values, the second recipe gave the best results (acid pH value is 9.4).

It was observed that the TPH content, pH values, and other indicators, including the concentrations of various metals in the initial tar, affect the efficiency of the stabilization recipe applied. All these efforts culminated in the acquisition of two patents: one international and one national. [15,16].

The literature suggests that the effectiveness of stabilization/ encapsulation technologies largely depends on the quality and intrinsic properties of the additives and binders used in the treatment recipes. This highlights the importance of selecting appropriate materials to achieve optimal performance in these technologies. [17-21].

Table 2. Encapsulation tar acid recipes

Ingredient	recipe 1	recipe 2	recipe 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

Discussions

The laboratory-scale application of the encapsulation stabilization technology of the acid tar and analysis of the experimental results may led to the following conclusions:

- Increasing the pH from values between 0.2 and 5.28 (in untreated acid tar) to values between 8.7 and 10 (in the leachate) positively impacted leaching performance, including the speciation of metal contaminants.

The highest concentration of TPH was detected in all acid tar samples, and at a depth of 30 cm, this concentration decreased by approximately fourfold. In the present study, Portland cement played a significant role in immobilizing Cr, Cu, and Pb. The degree of immobilization improved with increased curing time of the hardened material. The high pH of the cement facilitates the retention of metals as insoluble hydroxide or carbonate salts within the hardened structure. Additionally, calcium oxide and the emulsifier contributed to the transition of metals from a volatile phase to a stable phase. Specifically, the calcium oxide enhanced the immobilization of Cd, Cu, Ni, and Pb.

- The stabilization/encapsulation technology applied significantly reduced the mobility of cadmium, copper, chromium, lead, nickel, and arsenic in the acid tar, achieving a concentration decrease of over 95% for the target metals group (Pb, Cd, Cu, Cr, Ni).
- As observed in the published literature, the leaching of some heavy metals is largely influenced by the pH of the leachate. [14].

- Lead (Pb) concentrations ranged from 0.0003 to 0.0056 mg/kg in all stabilized samples.
- The pH of the samples from which metals were determined ranged from 8.7 (with a Pb content of 0.008 mg/kg) to 10.0 (with a Pb content of 0.002 mg/kg).
- Cadmium (Cd) concentrations in the eluate/leachate samples ranged between 0.0001 and 0.005 mg/kg.
- As mentioned in the literature, cement benefits Cd immobilization in all conditions [25].
- Copper (Cu) concentrations were found to vary from 0.00083 to 0.0161 mg/kg.
- Chromium (Cr), one of the most toxic metals, was measured in the eluate collected after acid tar treatment, with concentrations ranging from 0.0010 to 0.084 mg/kg.
- The immobilization of Cr^{6+} by the cement-based encapsulation/ stabilization technology was achieved through the formation of a complex calcium chromate ($CaCrO_4$), which has low solubility.

Nickel (Ni) concentrations in the eluate ranged from 0.0015 to 0.091 mg/kg dry substances. It was observed that Ni and Cd hydroxides are incorporated into the hydrated cement matrices, which provides effective immobilization for Ni.

- Arsenic (As) was distributed across a wide range of values in untreated tar, from 1.4 to 589 mg/kg dry substances, and in the eluate, from below 0.001 to 0.402 mg/kg.
- Cyanide concentrations in untreated acid tar ranged from 0.013 to 0.368 mg/kg dry substances, but in the leachate, they decreased to below 0.001, falling below the detection limit.
- There was a reduction in the concentration of chlorides, sulfates, and dissolved organic compounds (DOC) in the leachate.
- The DOC content ranged from 108 to 2047 mg/kg, with three values exceeding 1000 mg/kg.
- This research suggests that applying the stabilization and encapsulation process on a macro scale to acid tar with TPH values below 200,000 mg/kg would reduce the heavy metal content (Pb, Cd, Cu, Cr, Ni) and arsenic (As) to below the imposed limits and lower DOC to below 1000 mg/kg dry substance.

Table 3. Acid tar stabilization/encapsulation results

Acid tar	Leachate
• pH: between 0,2 and 5,28 • TPH between 48 333 and 477 062 mg/kg s.u. • Metals with values above the permitted limits: - Lead between 42 and 2235 mg/kg d.s. - Cadmium between 1 and 126 mg/kg d.s. - Copper between 2.6 and 789 mg/kg d.s. - Total chromium between 3 and 452 mg/kg d.s. - Nickel between 2 and 859 mg/kg d.s. - Arsenic between 1.4 and 589 mg/kg d.s. • Cyanides with values between 0.013-0.368 mg/kg d.s.	• pH: between 8.7 and 10.0 •THP between 263 and 3009 mg/kg •Metals with values above the permitted limits: - Lead between 0.0003 and 0.0056mg/kg - Cadmium between 0.0001-0.0050 mg/kg - Copper between 0.00083 and 0.0161 mg/kg - Total chromium between 0.0010 and 0.084 mg/kg - Nickel between 0.0015-0.091 mg/kg d.s. - Arsenic between LQ and 0.402 mg/kg d.s. • Cyanidess with values <0.001 (LQ) • Chloride content between 9.08 and 844 mg/kg • Sulphate content between 54.01 and 618.9 mg/kg • DOC between 108 and 2047 (with 3 values above 1000 mg/kg)

In conclusion, the effectiveness of the treatment for the studied acid tar is evident from the fact that the initial acid tar contained levels of representative contaminants above the maximum allowed limits. In the stabilized leachate, however, these values were significantly reduced, with some even falling below the quantification limits of the determination methods (Table 3).

CONCLUSIONS

In the literature, there are partial data on the pH, the content of hydrocarbons and heavy metals in the contaminated soil in the area of oil refineries, and even less in the acid tars.

There are no data available on the level of hydrocarbon and heavy metal concentrations in the acid tar lagoons, before the remedial treatment, and these data are almost completely missing for the lagoons subjected to the remedial processes.

Additionally, there is limited information on organic leaching from acid tars following the application of stabilization/encapsulation technology, as well as on the effects of organics on complex setting reactions that may alter the cement matrix.In this article, all these previously mentioned aspects are

covered, associated with data regarding the application of original recipes for the stabilization/encapsulation of acid tars from refinery lagoons.

The article presents scientific information published for the first time regarding the correlation of pH values with the concentrations of TPH and heavy metals (Pb+Cd+Cu+Cr+Ni) and As following the application of a complex process of neutralization, stabilization and encapsulation of acid tar from lagoon from a refinery in Romania.

To emphasize that the correlation of the pH, of the TPH content with the level of heavy metals and As in a lagoon allow the extrapolation and application of this stabilization - encapsulation procedure on a macro-in situ scale and the remediation of the lagoon where the acid tar was stored.

EXPERIMENTAL

In this paper, the experimental program involved the following steps:

- collection, codification and preparation of acid tar samples for testing (Figure 9);
- characterization of the initial samples;
- sample homogenization;
- performing chemical tests (determination of pH, TPH and heavy metal content);
- carrying out treatability tests;

a)   (b)

Figure 9. Acid tar, (**a**) sampling area; (**b**) acid tar sampleanalysis, evaluation and validation of treatability test results by performing leaching tests.

- Conducting tests by mixing reactants with acid tar samples and preparing formulations for subsequent testing;
- optimization of the mix design and selection of the mix design verification phase (from three recipes);
- preparation of the final mix design and performing treatability testing.

Considering the area of the site (a lagoon surface area of about 100 000 m^2), a number of 82 sampling points were chosen for the 2 depths (41 samples each for the two depths of 5 and 30 cm, respectively), which corresponds to the need for proper characterization of the acid tar on site. The acid tar samples were collected in boxes on which the sampling depth and the sample number were noted (Figure 9).

For the collection of acid tar samples from the depth of 5-30 cm, sampling probes was used a standard *auger set (*with *bayonet connection).* Once the samples were collected, proper homogenization were performed prior to initial (baseline) characterization.

In this phase, the experimental data were statistically analyzed using artificial intelligence (Data Science) to accurately predict the properties of acid tars from waste lagoons and their associated leachate. Additionally, the authors developed a software program employing Machine Learning to estimate key properties of acid tars, such as pH, total petroleum hydrocarbons (TPH), metals, and cyanides. The program evaluates five Machine Learning models (Linear Regression, Ridge, Lasso, Elastic Net, and Decision Tree) and selects the one with the best accuracy, as indicated by the Mean Absolute Error [24]. Given the high values of the mentioned indicators (pH, TPH, metals, and As) exceeding legal limits, several recipes were formulated, prepared, and tested. Ultimately, three representative recipes were selected (Table 2). After each recipe was applied, the acid tar samples were homogenized, mixed, and tested. Based on the values of TPH, pH, and metal concentrations, one of the recipes listed in Table 2 will be applied. The three formulated recipes are distinguished by:

- Constant concentrations of strengthening additives, absorbent, and sodium hydroxide (approximately 1% each)
- Variable amounts of emulsifier, synthesized at 1%, 3.5%, and 4%
- Increasing cement concentration, ranging from 3% in recipe 1 to 8% in recipe 3
- Variable concentrations of calcium oxide, from 8% in recipe 1 to 7% in recipe 3

- Increasing 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).

Batch leaching test: The validation of the proposed recipes for acid tar was conducted by ensuring that the indicators of the leachate/eluate from the treated acid tar met the maximum values allowed for leachate as specified by Order 95/2005. The leaching test was performed according to SR EN 12457-2/2003 – Waste Characterization: Leaching – Compliance Verification Test for Granular Waste and Sludge Leaching. This test involved contacting the waste sample with a leaching agent (water) at a mass ratio of waste/leaching agent (L/S) = 10 l/kg, maintaining this contact for 24 hours, separating the leachate, and analyzing the eluate to determine the relevant indicators.

Analytical determinations on the collected samples were carried out 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 matter and water content relative to mass. gravimetric method,
- SR EN ISO 9377-2-2002 – Water quality. Determination of the hydrocarbon index,
- SR ISO 10523:2009- Determination of pH,
- Method EPA413.2 and 418.1 ASTM, method D7066-04-Total content of hydrocarbons C10-C40 HP by I|R spectrometry with the INFRACAL 2 analyzer,
- SR EN ISO 15586:2004-Determination of trace metals by atomic absorption spectrometry with a graphite furnace,
- SR ISO 11047/1999-Determination of lead with flame atomic absorption spectrophotometer Xplor AA Dual GBS Scientific,
- Determination of the content of heavy metals with a mobile EDXRF spectrometer with X-ray detection for the rapid detection of trace elements from Mg (Z = 12) to U (Z = 92),
- ASTM D 516-2016-Determination of sulphates with UV-VIS spectrometer DR 3900 Hach,
- SR ISO 9297: 2001-Determination of chlorides with UV- VIS spectrometer DR 3900 Hach
- Determination of cyanides content with UV - VIS spectrometer DR 3900 Hach.

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