Treatment of Tar Wastes using the Envirotreat Process / Technology

Generic Overview

Envirotreat

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The following report has been based on results obtained from the treatment of an acidic tar waste from a site based in the north-west of the country. The waste consists of an acid sludge, spent clays (i.e. Fullers Earth containing absorbed heavy oil) and numerous chemical drums of unknown origin and content. The acid tar ranged in pH from 1.4 to 4.0, whilst the contaminated bentonite had a pH value ranging between 4.8 and 8.3.

Historically, acid tar lagoons are difficult to treat using conventional remediation technologies because of the acidic and toxic nature of the waste. Disposal options, such as landfilling or incineration are impractical and prohibitively expensive, and the production of volatile organic compounds (VOCs) during excavation of the tarry material is of particular concern. Furthermore, transportation of the waste through local settlements is also of concern. Notwithstanding these issues, disposal of acid tar in landfills is not intended to be the best practicable environmental option, since there is a proven potential for long term problems (Department of the Environment, 1986). Therefore, in order to address the remediation of the site, a modern, innovative solution to the problem is required.

For the treatment of complex and problematical hazardous wastes such as acid and alkali tar lagoons, the Envirotreat E-Clay Technology is a proven, cost-effective with predictable time scales and outcomes remediation process.

The Envirotreat E-Clay Technology

The Envirotreat E-Clay Technology is an advanced, chemical fixation / immobilisation process, applying proprietary modified-smectite clays (E-clays) to a broad range of contaminants resident in both soil and groundwater. These contaminants include organic and inorganic pollutants and heavy metals. The technology has been demonstrated for a diverse environmental application. It is applicable either *in-situ*, as part of a mass treatment and / or active containment system (ACS – Permeable Reactive Barrier), or *ex-situ* with the use of a standard plant and equipment to achieve treatment. The Envirotreat E-Clay Technology offers a sustainable and cost-effective approach to remediating contaminated land, which enables re-development to take place within a short and realistic time-scale.

The E-Clays incorporate various reactive species including combinations of transition metals, quaternary ammonium ions (QAS) and pillaring agents. The intercalation of these species within the clay structure installs a reactive environment, which can effectively absorb and chemically immobilise the target pollutants, in an irreversible chemical stabilisation process.

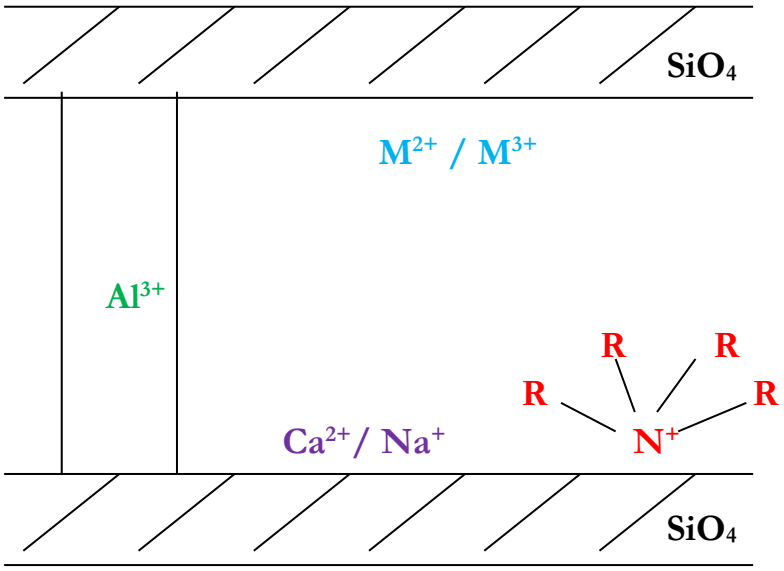
The E-clays can be used in conjunction with conventional stabilisation / solidification media, typically cementitious and/or pozzolanic materials, to produce a physically stabilised and solidified treated mass. The E-clays can also be used in ACS or for the direct treatment of ground or surface water; in this application, the pillaring effect promotes the passage of contaminated water through the clay matrix, wherein the pollutants are removed and absorbed, followed by chemical immobilisation within the structure. The pillars also contain reactive species, which are particularly appropriate for the treatment of anionic metallic species, in addition to treatment of organic species. The enlarged spacing created by the pillaring effect also acts to optimise the effective surface area available within the interlamellar increasing the potential reactivity of the E-clay.

The use of these reactive species in any particular E-Clay formulation depends on the nature of the target contaminants and the site-specific details. For example, the formulation of both organophilic (organoclay) and inorganophilic (inorganoclay) E-Clays is possible. The resulting organoclay provides an interlamellar environment of varying polarity to attract the organic portion of the targeted pollutant by absorption/adsorption processes and interaction with other relevant intercalated species. The resulting inorganoclay provides an active medium for the immobilisation of cationic and anionic heavy metals, by interaction with relevant intercalated species and/or by cation exchange processes on the clay surface and

pillars. By purposely designing a mix of E-Clay formulations on a site-specific basis, it is possible to immobilise a wide range of organic and inorganic/heavy metal contaminants, reducing the overall toxicity of the waste to within internationally recognised standards. Where appropriate, the E-Clay technology can be further refined to produce a 'combined' clay designed to treat both types of pollutant groups. This type of E-clay is referred to as an inorgano-organoclay, which can be either pillared or non-pillared.

Figure 1 shows a diagrammatic illustration of generically modified-pillared organo/inorgano clay, the specifics of which depend upon the application. This E-clay will react with both organic and inorganic contamination using a combination of chemical bonding techniques with the reactive intercalatants, and also control the acidity of the system.

Figure 1 - A Diagrammatic Illustration of a Modified, Reactive Pillared-Inorgano-/Organoclay



Al^{3+} Hydroxy Aluminium Pillars
Ca^{2+} / Na^{+} Residual Cations
M^{2+} / M^{3+} Transition Metal Complexes
N^{4+} Quaternary Ammonium Salts

Mass Treatment Approach

The tar itself is relatively inert. However, the presence of mobile and toxic pollutants within the tar waste, including tar breakdown products, engenders a high capacity for the waste material itself to continually generate a toxic and highly mobile leachate containing priority pollutants.

The treatment trials undertaken, refined the E-Clay formulation and addition rates to produce an optimum treatment mixture. Only data from the final mix composition has been incorporated into this report. The mass treatment trials incorporated E-Clays as well as cement. The trials were performed on both tar and bentonite samples and the results can be seen in the following Table 1.

Following discussions with the regulators, it was agreed to utilise a modified NRA (current industry standard leaching methodologies are still based on this approach) leaching test protocol for validating the successful chemical immobilisation of contaminants using the Envirotreat E-Clay Technology. The modified NRA leaching protocol totally breaks down the stabilised mass (complete disintegration) giving a worst-case scenario in respect of leachability. This test has been utilised by Envirotreat on a contractual basis and addressed the relevant components of both the unmodified NRA and American TCLP test. We have therefore, used the modified NRA leachate test to produce the results contained in this report.

Table 1 - Leached Stabilised Samples; Mass Treatment Approach

Sample ID	**Control Leachate**	**Stabilised Tar Sample (Leachate)**	**% Removal**	**Stabilised Bentonite Sample (Leachate)**	**% Removal**
Analyte					
Arsenic	0.025	<0.005	>80	<0.005	>80
Cadmium	0.007	0.001	86	0.002	71
Chromium	0.36	0.02	94	0.18	50
Copper	0.47	0.14	70	0.11	77
Lead	0.15	<0.05	>67	<0.05	>33
Nickel	0.54	0.06	89	0.07	87
Zinc	2.6	0.18	93	0.16	94
Cyanide	<0.05	<0.05	100	<0.05	100
Phenol	0.05	<0.05	100	<0.05	100
Sulphate	N/A	2,770	--	1,860	--
TPH	562,890	2,390	99.5	3,395	99.4
Iron	172	0.23	99.9	0.03	99.9
Manganese	2.9	0.06	98	0.11	96
Total Heavy Metals*	179.05	0.746	99.58	0.717	99.996

All analytes expressed as mg/l

Total Petroleum Hydrocarbons expressed as µg l

*Sum of the values for arsenic, cadmium, chromium, copper, lead, nickel, zinc, iron and manganese

Percentage removal rates for the prime pollutant group of concern was shown to be 99.5 for the tar sample and 99.4 for the bentonite sample. The other pollutants were also removed to satisfactory levels using the Envirotreat E-Clay Technology. Overall removal rates for total heavy metals significantly

exceeded the 95% target value, although certain individual metal results were on face value, not as high as the identified minimum target value of 85%, these being arsenic, copper and lead for both samples and cadmium and chromium for the contaminated bentonite sample only. The values for arsenic and lead reflect the minimum detectable levels and consequently the actual removable rate could well be significantly higher than those stated above. The results for cadmium, chromium and copper are still very low and it is not considered that these pollutants represent a significant environmental risk at these concentrations. In both cases the phenol results were very satisfactory (both >95%).

It is evident from the above results that the prime pollutant of concern is TPH, which encompasses a broad range of both oil-based soluble organic pollutants. It was therefore decided to focus the next stage of leachate testing on TPH, with the objective of evaluating the capability of the technology to address the full range of tar-bearing wastes identified on-site, with the attendant wide variation in physical properties etc.

Table 2 - TPH Results for Leached Samples after Optimisation; Mass Treatment Approach

Sample Code	**Sample Position (Depth below surface)**	**Total Petroleum Hydrocarbons (µg/l)**	**% Removal Rate**
Control (Untreated Leachate)		562,890	
*	1,000mm	6,940	98.8
*	2,000mm	2,760	99.5
*	4,000mm	3,260	99.4

The results showed a substantial reduction in TPH for the samples stabilised using the optimum mix, achieving greater than the 95% target level. These optimisation trials illustrate that even the more problematical pollutants within the tar wastes can be satisfactorily addressed using a combination of E-Clays and cement. In practice, the remediation process would involve substantial integral mixing of the tar layers thus producing a more homogeneous tar substrate material than would be the case if the tar layers were left undisturbed. It is therefore reasonable to presume that an optimum E-Clay / cement mix will suffice for the treatment of the tar wastes as a whole.

It is only by incorporating a mixture of E-clay and cement that the acidic nature of the system was addressed. Both additives are alkaline and contribute to the elevation of the overall pH of the tar / bentonite.

In summary, the results achieved demonstrate the efficacy of the treatment approach incorporating optimum addition rates of E-Clays and/or cement for the successful chemical immobilisation of the identified pollutants within the tar waste. Envirotreat's proprietary technology can be applied to both chemically and physically stabilise the tar and contaminated bentonite, essentially rendering the material inert. The improvement in physical properties associated with the mass treatment approach will enable the treated tar waste to be both physically and chemically immobilised.

Proposed Active Containment System Approach (PRB)

Assessing the efficacy of the proposed ACS (PRB) entailed a number of treatment trials. Whereas the mass treatment approach deals with the solid material, the tar and bentonite, the ACS is designed to treat ground water and leachate. Both elements of the remediation strategy are designed to function synergistically to produce an effective solution for the site as a whole.

A control leachate was produced from combining all tar sample leachates (1:1, water : solid solution). This 'stock leachate solution' is intended to mimic the conditions, which may materialise as a consequence of the tar wastes contacting water, thereby generating a contaminated leachate. This leachate has the potential to migrate off-site and is therefore a potential pollution risk. The sample of stock leachate solution was substantially more contaminated than the actual ground water on site and therefore represents a worst case scenario for determining the suitability of the E-clays in the proposed ACS. The results from direct treatment of the stock leachate solution, using the optimum ACS modified pillared E-clay mix composition are as shown in the Table.

Table 3 - Treatment of Leachate Utilising Modified Pillared E-clays; ACS Approach

Sample ID	**Control**	**Test**
Analyte		
Arsenic	0.025	N/A
Cadmium	0.007	0.010
Chromium	0.36	0.08
Copper	0.47	0.73
Lead	0.15	0.13
Nickel	0.54	1.5
Zinc	2.6	1.3
Cyanide	<0.05	N/A
Phenol	0.05	N/A
Sulphate	N/A	800
TPH	562,890	7870
Iron	172	36
Manganese	2.9	0.90
Total Heavy Metals*	179.052	40.65

All analytes expressed as mg/l

Total Petroleum Hydrocarbons expressed as µg/l

*Some of the values for arsenic, cadmium, chromium, copper, lead, nickel, zinc, iron, and manganese.

The results for the treated leachate clearly demonstrate successful removal of TPH and other pollutants contained within the leachate sample. The TPH results show a percentage reduction of 98.6%, whilst total heavy metal results show a percentage reduction of 77%. It should be noted that the results for individual heavy metals showed some fluctuation, which can only be attributed to analytical error at low concentrations (for example, the value for nickel in the treated sample is three times the value for the untreated, which clearly cannot be the case as the modified clays would not in any way have increased the heavy metal content of the treated leachate).

Physical Properties

Envirotreat used the unconfined compressive strength (UCS) tests to establish the structural integrity and projected stress load of the stabilised material. The results included in this report for UCS are those for optimum E-Clay / cement mix compositions.

The test protocol is as follows. The sample mix is placed in a PVC mould, ensuring that as little air as possible is trapped in with the mix. The mould is filled to the top with the mix and levelled. The mould's dimensions are nominally 71 mm in diameter and 142 mm high, which is the standard ratio for UCS tests giving a height to diameter ratio of 2:1. The stabilised mix is then left to cure for a period of 28 days.

Once cured, a vertical slit down one side of the mould facilitates easy extraction of the sample from the mould. A vertical load is applied to the top of the sample via a loading ram at a rate of 1 mm/min using a triaxial testing machine. The load is applied through a proving ring and monitored by a dial gauge throughout the test. When the sample buckles and cannot support further load, the sample is said to have failed. The value of the load at the point of failure is then divided by the cross-sectional area of the sample to give a value for UCS.

UCS tests are generally used as an indicator of the effectiveness of stabilisation / solidification technologies. The term 'unconfined', refers to the sample which is not constrained horizontally during the test, i.e. there is no horizontal loading applied to the sample. This is particularly relevant for tar lagoons, where there is a propensity for the tar to move laterally under vertical pressure. Once fully treated, the real life *in-situ* stabilised mass will be constrained horizontally (by the rest of the treated mass) and under these circumstances, it is a reasonable assumption that the treated mass will have a greater ability to support vertical loading than demonstrated by this test.

In addition, physical property tests were carried out in relation to hydraulic conductivity or permeability of the treated mass. In this respect samples were taken from the cured samples and tested in accordance with the standard specification as utilised by Envirotreat i.e. ASTM D2434.

The sample preparation stage for the permeability test is identical as for the UCS test described above. Once the stabilised samples have cured for the 28-day period, porous disks were placed at both ends of the sample. A cell pressure of 300 KN/m^2 was applied and then the sample was left for a period of 24 hours to reach equilibrium. Following this, the drainage taps were opened and the sample was left to consolidate for a further 24 hours. A constant flow rate was then introduced at the base of the sample producing an upward vertical flow of water through the sample via the use of a flow pump. Readings of the pore water pressure were taken at the inflow position using a pore pressure transducer. The pore water pressure within the sample was not allowed to exceed 20% of the cell pressure itself. Similar hydraulic gradients were employed in all of the tests. Once the pore water pressure reached equilibrium, the vertical permeability was calculated using Darcy's law.

To obtain a comparative overview of the permeability of the treated material, samples were chosen which reflected low, medium and high UCS values (representing in theory, varying degrees of homogeneity). The results included in this report for permeability therefore cover the full likely range of permeability values for treated tar samples throughout the lagoon.

Target levels for the physical properties of the ground after stabilisation reflect future land-use, in this case, landscaping or similar. A UCS target value of 80 KN/m2 is acceptable as this is the value normally required for residential developments.

The results are based on average results obtained from duplicate samples tested following stabilisation / solidification trials incorporating the optimum E-Clay / cement mix composition. The contaminated bentonite sample was stabilised and analysed as a separate entity from the other contaminated tar samples. For methodology, please refer to method statement.

Table 4 - Representative Results Illustrating UCS

Sample Reference	UCS value (KN/m2)
A	125
B	102
C	203
D	414
E	274
F	180
G	164
H	164
I	656
J	344

The UCS results were very impressive, bearing in mind that the tar material itself has varying physical properties in terms of viscosity and thixotrophy etc. All samples tested illustrated substantial improvements in UCS values following stabilisation / solidification (the tar itself had no integral strength and could not be tested using the standard protocol).

Having identified respective UCS values, selected samples were subsequently tested for hydraulic conductivity / permeability. These samples covered the full range of physical stabilisation in terms of UCS values.

Table 5 - Permeability Results

Sample Reference	Permeability (m/s)
L	8.0×10^{-8}
M	4.0×10^{-8}
N	1.5×10^{-8}

Target values for permeability for this type of application were stipulated to be no greater than 1×10^{-7} m/s. All of the samples achieved acceptable permeability levels.