



StabOx[®] E-Clay Technology – a Technical Summary

1.0 Introduction

The StabOx[®] technology combines E-Clay[®] chemical immobilisation [stabilisation] technology with chemical oxidation. This provides the additional capability to reduce the concentrations of organic pollutants immobilised within the clay matrix. E-Clay[®] and StabOx[®] are registered trademarks.

The application of chemical oxidation for the treatment of soil and groundwater contamination has been increasingly practised for over the past twenty years. Chemical oxidation offers significant benefits as the process rapidly destroys / degrades organic contaminants significantly reducing contaminant mass into less harmful breakdown products. The process has been extensively used for the destruction or degradation of a variety of hazardous wastes in groundwater, soils and sediments. The oxidants used are readily available and treatment times are relatively short making the process economically feasible. The common oxidants used for chemical oxidation include hydrogen peroxide, sodium percarbonate, sodium or potassium permanganate, sodium persulphate and ozone. Applied *in-situ* the treatment process has given significant contaminant mass reductions that have been observed at many sites for the treatment of contaminated soils and groundwater.

Treatment by chemical oxidation requires direct oxidant-contaminant interaction and is therefore subject to multiple interference from factors associated with site geology, hydrogeology, contaminant plume characteristics and matrix interaction effects which inhibit oxidation. As more sites have undergone treatment increasingly recurrence of dissolved phase contaminant concentrations has been found once treatment has been considered complete. This contaminant recurrence known as ‘rebound’ is now considered the norm following a single treatment process. It is now understood that in order to reach sufficient target treatment levels multiple applications of the chemical oxidation treatment process are often required.

This paper presents work carried out by Enviro-treat to develop advanced E-Clay products suitable for application to chemical oxidation treatment processes. This product range referred as ‘StabOx E-Clay’ has been developed from existing E-Clay technology, traditionally used for the chemical stabilisation of contaminants. By modifying existing E-Clay technology the StabOx products offer treatment of organic pollutants by chemical oxidation combined with chemical stabilisation (immobilisation) processes. By combining both technologies within one product we have a multi-capability technology which can effectively deal with organic pollutants (oxidisable or not). The StabOx technology can also be applied for the treatment of both organic and inorganic pollutants offering additional benefits to the process.

The use of an E-Clay matrix for the StabOx product offers increased stability to the process as the oxidant can be added *in-situ* at the contaminant source point in a solid clay-based form. The clay matrix ensures that once the product is installed in the environment the oxidant is less susceptible to interfering factors associated with site geology etc. that can inhibit the oxidation process. The effects of contaminant rebound can be better managed reducing the need for multiple applications of the treatment process.

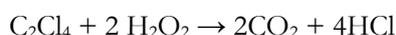
2.0 Chemical Oxidation Treatment Technology

The basic principles of chemical oxidation use redox (reduction-oxidation) reactions to breakdown contaminants into less hazardous by-products. During chemical oxidation reactions atoms have their oxidation number (oxidation state) changed. This can be a simple process such as the oxidation of carbon to yield carbon dioxide or the reduction of carbon by hydrogen to yield methane.

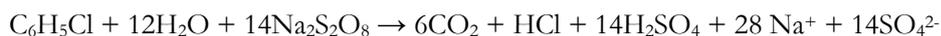
Chemical oxidation involves the loss of electrons or an increase in oxidation state. Conversely chemical reduction involves the gain of electrons or a decrease in oxidation state.

In the chemical oxidation treatment process electrons are transferred from the contaminant to the oxidant. As a result the contaminant becomes oxidised (with the breaking of chemical bonds) and the oxidant becomes reduced as it receives electrons. Common oxidants used for chemical oxidation include hydrogen peroxide (H₂O₂), sodium percarbonate (Na₂CO₃·1.5H₂O₂), potassium permanganate (KMnO₄), sodium persulphate (Na₂S₂O₈) and ozone. Examples of oxidation reactions using such oxidants are provided below:

- ❖ Hydrogen peroxide oxidation of tetrachloroethene [PERC]:



- ❖ Sodium persulphate oxidation of monochlorobenzene [MCB]:



- ❖ Potassium permanganate oxidation of tetrachloroethene [PERC]:

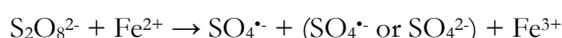


The reactions demonstrate complete oxidation of the hydrocarbon contaminants PERC and MCB producing less hazardous breakdown [daughter] products from oxidation of the parent contaminant. For example, the potassium permanganate oxidation of PERC produces carbon dioxide, potassium chloride and oxygen. In order to completely oxidise hydrocarbon contaminants to carbon dioxide all chemical oxidants must either supply oxygen itself or from reactions with water. To facilitate or enhance this process a catalyst is often included to bring about free radical oxidation and reduction. A free radical is a highly reactive molecule having an unpaired electron. Free radicals are therefore highly conducive to redox processes.

Some metals have a strong catalytic power to generate free radical formation. The use of ferrous iron in combination with hydrogen peroxide (known as Fenton's Reagent) is widely accepted as an established chemical oxidation technology for the treatment of hydrocarbons. Chemical oxidation using Fenton's reagent requires soluble ferrous iron (Fe²⁺) to react with hydrogen peroxide forming hydroxyl radicals (OH•) with optimal reaction conditions of pH 2 to 4 i.e.



Similarly sodium persulphate can be activated by addition of ferrous sulphate. The addition of ferrous iron induces the formation of sulphate radicals which is one of the strongest aqueous oxidising species i.e.



The selection of oxidant depends on numerous factors associated with site characteristics, contaminant type and contaminant plume characteristics. For example, hydrogen peroxide is widely used for treatment of VOCs and permanganate salts are considered best suited for treatment of alkenes, aldehydes, alcohols and methyl ketones. Persulphate salts are suitable for chlorinated hydrocarbons while Fenton's Reagent has a wide range of applications although subject to many interferences. A comparison of the effectiveness of each oxidant is provided in Table 1 below.

Table 1 - Effectiveness of the Oxidants

Contaminant	Activated Peroxide (Fenton's Reagent)	Percarbonate	Permanganate	Persulphate	Activated Persulphate
Petroleum Hydrocarbons	√√√√	√√√√	√√√	√√√	√√√
Benzene	√√√√	√√√	√	√√√	√√√
MTBE	√√√	√√√	√√√	√√	√√√
Phenols	√√√√	√√√	√√√	√√	√√√
Chlorinated Ethenes (DEC, PCE, TCE, VC)	√√√√	√√√√	√√√√	√√√	√√√√
Chlorinated Ethanes (TCA, DCA)	√√√	√√√	√√	√	√√
Polycyclic Aromatic Hydrocarbons (PAHs)	√√√√	√√√	√√√	√√√	√√√√

Key:

- √√√√- Short treatment time, low energy requirement, most complete oxidation
- √√√- Intermediate treatment time, low energy requirement, intermediate degree of completion
- √√- Intermediate treatment time, intermediate energy requirement, low degree of completion
- √- Long treatment time, high energy requirement, very low degree of completion

3. StabOx E-Clay Treatment Technology

E-Clays are modified smectite clays commercialised by Envirotreat Technologies. Originally developed for the treatment of organic pollutants using chemical stabilisation techniques, E-Clays have been adapted for the treatment of inorganic species and radionuclides, either in isolation or in combination with the treatment of organic pollutants.

Partial modification of normal bentonite clay produces a pillared inorganoclay with the capability of sorbing and chemically reacting with both cationic and anionic species. This form of inorganoclay is produced by the controlled stoichiometric intercalation of hydroxyaluminium cations. The hydroxyaluminium species react with anionic forms such as permanganate (MnO_4^-) and persulphate ($S_2O_8^{2-}$) binding the anionic species to the clay – this is shown schematically in Figures 1 and 2 below.

Further modification of the inorganoclay with a quaternary ammonium salt (QAS) reactive agent produces an inorgano-organo E-Clay (first developed by Envirotreat for the chemical stabilisation of organic pollutants). The addition of QAS to the E-Clay matrix produces an organophilic environment which attracts and binds hydrocarbon pollutants to the clay matrix – see Figure 3 below. The degree of organophilic property of the E-Clay can be controlled by the degree of intercalation of the designated QAS to the clay matrix.

Hydrogen peroxide can be effectively incorporated into the matrix enabling reactions with the hydrocarbon pollutants previously sorbed and immobilised within the matrix. This necessitates a two-stage StabOx process.

The StabOx E-Clay technology enables the effective treatment of both oxidisable and non-oxidisable organic pollutants using one treatment product.

Using chemical oxidation combined with chemical stabilisation the StabOx E-Clay technology can effectively treat problematic hydrocarbon pollutants such as benzene that are traditionally resistant to complete chemical oxidation.

The StabOx E-Clays also have affinity for cationic species (typically heavy metal pollutants such as copper, lead and zinc). Cationic species preferentially exchange at residual reactive sites on the clay, displacing Ca^{2+} and/or Na^{+} cations from the original bentonite clay matrix. It is also possible to treat anionic pollutants such as CrO_4^{2-} and AsO_4^{3-} by chemical interaction with the aluminium pillars.

Figure 1 – Schematic Illustration of StabOx E-Clay - Intercalation of Permanganate Ion [MnO_4^-]

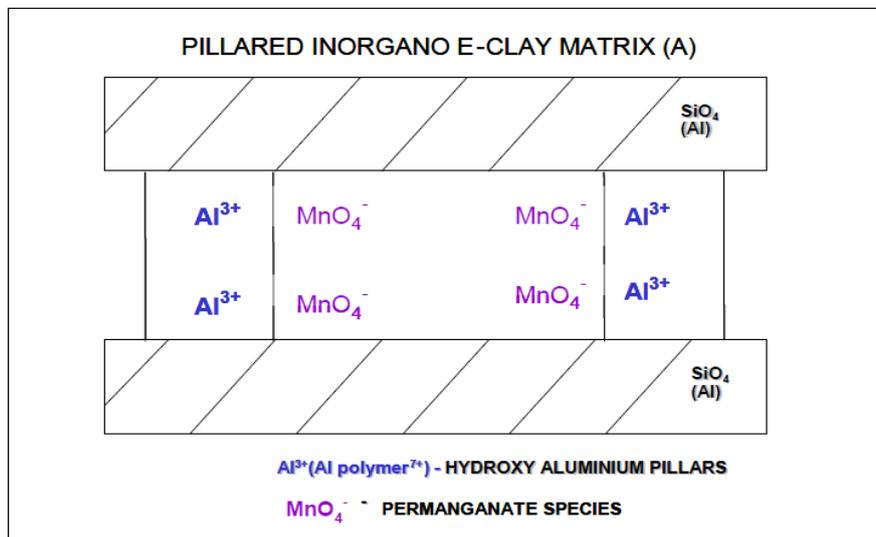


Figure 2 – Schematic Illustration of StabOx E-Clay - Intercalation of Persulphate Ion [$\text{S}_2\text{O}_8^{2-}$]

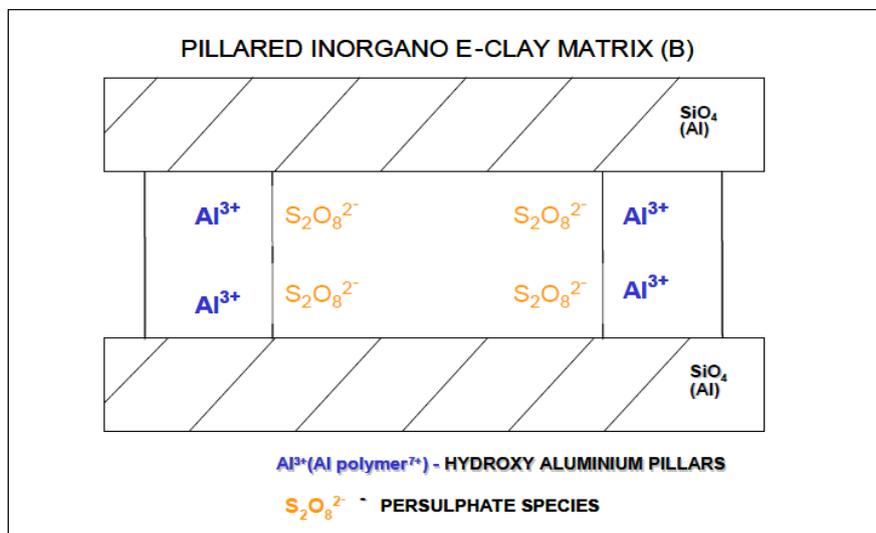
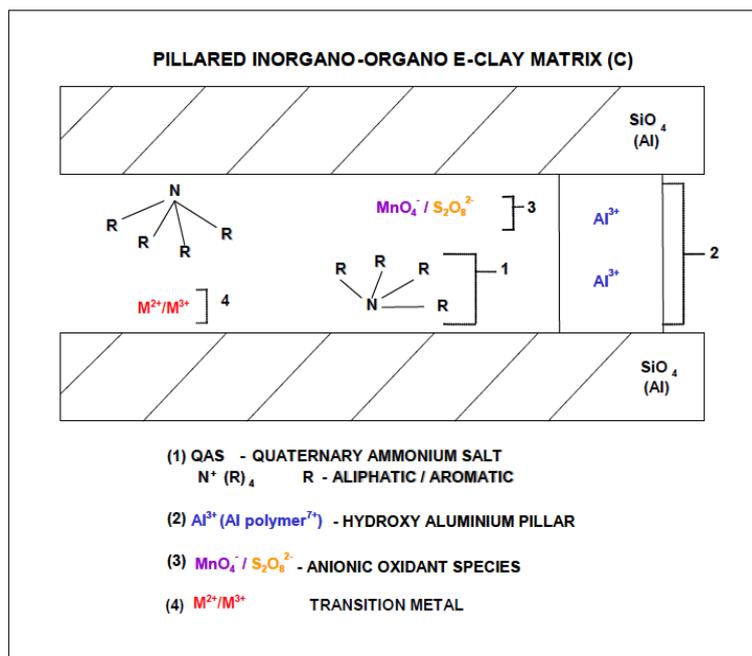


Figure 3 – Schematic Illustration of StabOx E-Clay (Pillared Inorgano-Organoclay)



3.1. Application of Envirotreat StabOx E-Clay Technology

The Envirotreat E-Clay technology can be applied *in-situ* for the treatment of contaminated soils and groundwaters and *ex-situ* for the mass [source] treatment of contaminated materials. The E-Clay matrix provides an effective carrier for the oxidant species providing a stable matrix with increased control over contaminant-oxidant interaction within the subsurface. The application of StabOx E-Clay technology avoids the need for excess chemicals and when handled appropriately does not have the health and safety concerns and lingering environmental issues that have become associated with some chemical oxidation technologies.

When applied *in-situ* the E-Clays are added using either advanced continuous flight auger soil mixing techniques or by trenching techniques depending on the application. In this way the StabOx E-Clays can be used for source treatment of contaminants or for treatment of groundwater by the installation of a permeable reactive barrier [PRB]. The barrier systems are designed to intercept contaminated groundwater and treat the contaminants as the groundwater migrates through the barrier.

Applied *ex-situ* the process involves the excavation of contaminated material using conventional civil engineering plant and equipment. The contaminated material is stockpiled prior to treatment and then transferred to a treatment zone. The contaminated materials are then mixed with a treatment slurry (containing E-Clays and cementitious materials if required). This treatment process produces a homogenous treated mass, which is chemically and if cement is used, physically stabilised. Following the treatment process, the material is either temporarily stockpiled or transferred directly to the designated site of deposition.

4.0 StabOx E-Clay Development and Treatment Trials

A number of laboratory treatability trials were carried out to develop a StabOx E-Clay product range. These trials were carried out at the Envirotreat Analytical and Development laboratory facility located Kingswinford, West Midlands. The permanganate and the persulphate oxidants were chosen for StabOx E-Clay production.

Permanganate was considered to have advantages over other oxidants such as the capability to oxidise over a wide pH range and react over a prolonged period in the subsurface allowing the oxidant to effectively contact absorbed contaminants. The use of permanganate does not present major health and safety concerns.

Persulphate was considered advantageous as the oxidant is capable of performing direct oxidation utilising the persulphate ion itself and also performing oxidation by sulphate free radicals which also have associated advantages over other oxidants. The ferrous sulphate catalyst was incorporated into the trials to activate the StabOx E-Clays and assist with free radical oxidation.

4.1 StabOx E-Clay Production

The initial focus of the trials was to produce or manufacture E-Clay suitable for application to chemical oxidation. The StabOx E-Clays were produced using pillared inorgano E-Clays with modification to incorporate the oxidant species. The StabOx products were prepared by addition of the oxidant to slurry suspension of pillared inorganoclay. The resultant mixture was stirred for sufficient time to allow for intercalation of the oxidant species to the E-Clay matrix and the mixture was then filtered to remove excess water leaving the StabOx E-Clay product.

4.1.1 E-Clay Intercalation of Reactive Oxidant Species

To produce a stable product suitable for application in the field it was important that the oxidant species was absorbed and retained by the E-Clay matrix. The first step in the development process was to determine that the anionic oxidant species (MnO_4^- and $\text{S}_2\text{O}_8^{2-}$ respectively) were intercalated into the E-Clay matrix by chemical interaction with the aluminium pillars of the E-Clay as described in Section 3 above. This was an important step as the nature and degree of bonding of the anionic oxidant species to the E-Clay was crucial to the success of the product. To this end a series of StabOx products were prepared ranging from a non-pillared E-Clay to a highly pillared E-Clay. The addition rate of oxidant was kept constant for each product and the amount of oxidant taken up by each E-Clay was measured to determine uptake efficiency. Measurement of oxidant uptake was determined by analysis of filtered E-Clay slurry solutions (filtered through 0.45 μm membrane filter paper to remove all traces of clay). Oxidant analysis was carried out at the Envirotreat Analytical & Development facility using ICP-AES for manganese determination for the permanganate oxidant and sulphur determination for the persulphate oxidant.

4.2 StabOx E-Clay Treatability Trials

Treatment trials were performed in the laboratory to evaluate the treatment efficacy of the StabOx E-Clays. To demonstrate treatment of non-chlorinated hydrocarbon pollutants the E-Clays were batch tested against phenol, BTEX and diesel fuel oil contaminants. To demonstrate treatment of chlorinated hydrocarbon pollutants the E-Clays were batch tested against a mixture of chlorinated phenols and trichloroethylene (TCE).

For each batch test StabOx E-Clay was added to laboratory prepared hydrocarbon contaminant mixtures and mixed for 24 hours. Each batch test was carried out in a glass vial capped with a PTFE lined septum to minimise losses of hydrocarbon by volatilisation and ensure that any observed reductions in contaminant concentration were as a result of chemical oxidation. All analysis was carried out at the Envirotreat Analytical & Development facility, with phenol measured by Palintest Total Phenol determination, BTEX by headspace analysis with GC-FID, diesel fuel by liquid/liquid extraction and analysis by GC-FID and TCE by headspace analysis with GC-FID.

5.0 Results and Discussion

5.1 StabOx E-Clay Production Trials

As previously discussed the StabOx E-Clay products were prepared using a permanganate oxidant and also a persulphate oxidant. A sample of permanganate StabOx E-Clay product is illustrated in Figure 4 below – this photograph shows the filter cake product obtained from the filtered slurry mixture produced according to methodology given in Section 4 above. To act as a chemical oxidant it was essential that the permanganate oxidant was bound to the E-Clay with the manganese ion in its highest oxidation state [Mn(VII)]. This would be indicated by a purple colour of the clay associated with Mn⁷⁺ ions present in the reactive permanganate species [MnO₄⁻] (*N.B.* in the reduced non-reactive form a brown colouration would be observed associated with Mn²⁺ ions of manganese dioxide [MnO₂]). Figure 4 shows that permanganate was successfully retained with manganese in its highest oxidation state illustrated by the intense purple colouration of the clay produced by Mn⁷⁺ ions of the permanganate species. The picture was taken some 2 weeks after the clay was produced demonstrating stability of the product to retain manganese in oxidised form.

Figure 4 – Photograph Showing StabOx E-Clay Incorporating Permanganate [MnO₄⁻]



5.1.1 E-Clay Intercalation of Reactive Oxidant Species

The oxidant uptake efficiencies determined for the StabOx E-Clay products are given in Table 2 below. Using this data it was possible to determine the effectiveness of the inorganoclay pillaring agent to oxidant uptake into the clay matrix.

The E-Clay formulation of each product tested is listed in the first two columns of Table 2. The degree of pillaring to the E-Clay is designated by 'Px'. For example, 'P10' indicates a 10% pillared clay while 'P40' indicates a 40% pillared clay. E-Clay 'P0' represents non-pillared clay with 0% pillaring. The data listed as mg/g represents mg oxidant per g E-Clay, while oxidant uptake efficiencies are given as a percentage. A higher addition rate of persulphate oxidant was used for the persulphate clay formulations as it was considered from literature review that more persulphate is required for effective oxidation compared to that of permanganate based on the % active oxygen contents of the two oxidants (15.2% active oxygen for permanganate and 6.7% active oxygen for persulphate respectively).

Table 2 - Oxidant Uptake by StabOx E-Clay Products

StabOx E-Clay Product	E-Clay Formulation	Oxidant Added (mg/g)	Oxidant Intercalated (mg/g)	Oxidant Uptake (%)
Permanganate Oxidant	P0	22.7	0.00	0.0
	P10	22.7	0.66	2.9
	P20	22.7	1.53	6.7
	P40	22.7	2.94	13
Persulphate Oxidant	P0	81.5	0.00	0.0
	P20	81.5	6.1	7.5
	P40	81.5	15.8	19
	P40 + FeSO ₄	81.5	19.9	24

The data clearly showed the effect of E-Clay pillaring to oxidant uptake. Importantly, no oxidant uptake was observed for the non-pillared clays [P0]. For permanganate oxidant formulation: 2.9% uptake was observed for the 10% pillared clay, increasing to 13% uptake for the 40% pillared clay. For persulphate oxidant formulation: 7.5% uptake was observed for the 20% pillared clay with 19% uptake observed for the 40% pillared clay. An additional activated persulphate oxidant formulation was tested containing the ferrous sulphate catalyst (formulation P40 + FeSO₄). Oxidant uptake was unaffected by the use of the catalyst salt.

This trial successfully confirmed that the mechanism of anionic oxidant species (MnO₄⁻ & S₂O₈²⁻) intercalation to StabOx E-Clay occurred by interaction with aluminium pillars of the pillared inorgano E-Clay as illustrated in Figures 1 – 3 above. As can be seen the percentage uptake of oxidant was found to increase linearly with increased pillaring of the clay demonstrating a clear correlation between the two factors. Confirmation of this mechanism was important for the production of a stable E-Clay product suitable for application to chemical oxidation treatment processes.

5.2 StabOx E-Clay Treatability Trials

Treatability trials were carried out to demonstrate treatment of non-chlorinated hydrocarbon pollutants and chlorinated hydrocarbon pollutants. The StabOx E-Clays were batch tested against phenol, BTEX and an aliphatic / aromatic hydrocarbon mixture to evaluate treatment of non-chlorinated hydrocarbons. To evaluate treatment of chlorinated hydrocarbons the E-Clays were tested against a chlorinated phenols mixture and trichloroethylene (TCE).

5.2.1 Non-Chlorinated Hydrocarbons

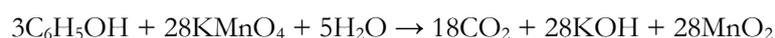
Chemical Oxidation of Phenol

The results for the batch test treatment of phenol are provided in Table 3 below. A permanganate StabOx product was used for this test. The results show that the StabOx E-Clay was highly successful in treating phenol with the relatively low addition rates of **0.5%** E-Clay achieving a **50%** treatment efficacy and the **2%** addition rate achieving greater than **99%** treatment efficacy. Addition of E-Clay above 2% reduced phenol to below detection level.

Table 3 - StabOx E-Clay – Batch Test Results - Chemical Oxidation of Phenol

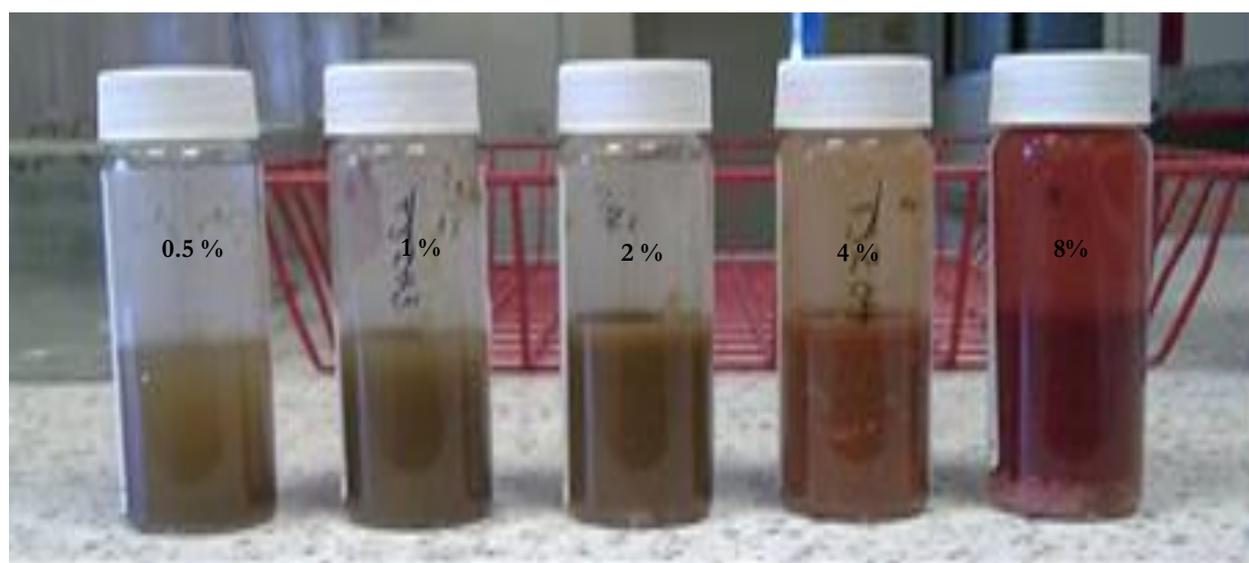
Phenol Treatment StabOx [®] E-Clay				
E-Clay Addition Rate (%)	Initial Conc. (mg/L)	Conc. at Equil. (mg/L)	Conc. Treated (mg/L)	Treatment Efficacy (%)
0	50	50	0	0
0.5	50	25	25	50
1	50	12	38	76
2	50	0.26	49.74	99.48
4	50	<0.01	49.99	99.98
8	50	<0.01	49.99	99.98

The batch test mixtures after the mixing process are shown in Figures 5 and 6 below - the unfiltered mixtures containing both E-Clay and test mixture are shown in Figure 5 and the filtered batch solutions are shown in Figure 6 below. The photographs are useful as they provide a clear colorimetric demonstration that chemical oxidation was the mechanism responsible for the treatment of phenol and that the StabOx E-Clay product performed as intended. For example, Figure 5 clearly shows a defined brown colouration from 0.5% to 2% addition changing to increasingly purple for the 4% and 8% addition rates respectively. The brown colour confirms the presence of manganese dioxide; MnO₂ [Mn²⁺] – generated by reduction of the purple permanganate ion; MnO₄⁻ [Mn⁷⁺] through reaction with phenol according to the equation below:



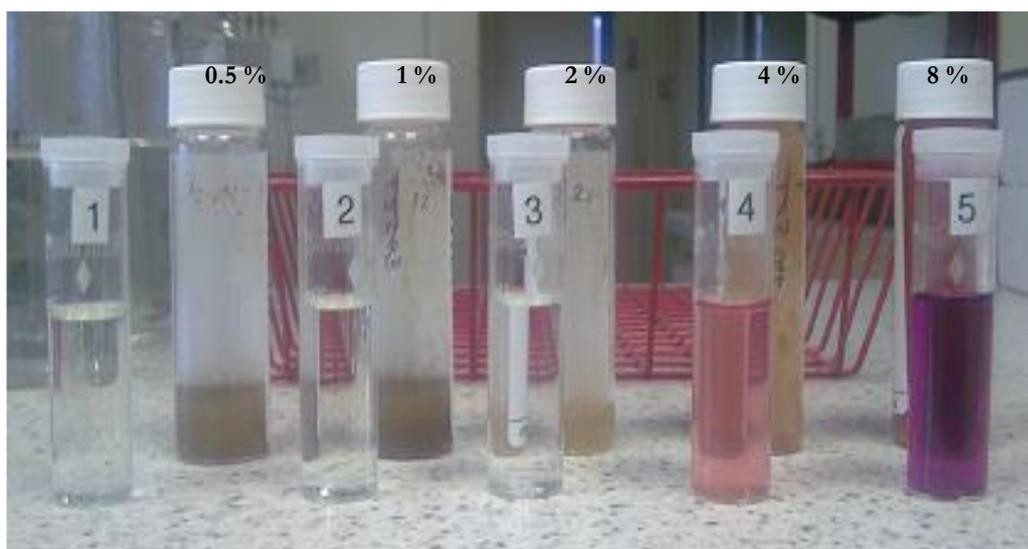
The purple colour in the 4% and 8% samples shows the presence of excess unreacted permanganate as all phenol in solution has reacted with the clay. This is confirmed by Figure 6 with the 0.5% through to 2% samples appearing colourless after filtration, with brown insoluble MnO₂ retained by E-Clay and unreacted MnO₄⁻ passing through the filter to give the purple colour in the 4% and 8% samples.

Figure 5 – Batch Test Mixtures – Chemical Oxidation of Phenol



Phenol batch test mixtures from left to right 0.5% to 8% addition rate StabOx E-Clay – brown colour indicates reduced or reacted permanganate, purple colour indicates excess unreacted permanganate

Figure 6 – Batch Test Mixtures – Chemical Oxidation of Phenol



Phenol batch test mixtures from left to right 0.5% to 8% addition rate StabOx E-Clay; unfiltered mixtures to rear, filtered solutions to front – reduced manganese (MnO_2) removed from solution tubes 1, 2 & 3 excess unreacted manganese (MnO_4) in solution tubes 4 & 5

Chemical Oxidation of BTEX

The results for the batch test treatment of BTEX are provided in Tables 4 and 5 below. Table 4 provides equilibrium solution data for the treated mixes and Table 5 lists treatment efficacies as a percentage. The batch tests were carried out using two concentration ranges of BTEX; a higher mix and a lower mix listed as Initial Conc. (untreated concentration) in the tables. The trial was carried out using both persulphate and permanganate StabOx E-Clay products. The ferrous sulphate catalyst was also added to activate the persulphate product for performance comparison.

Table 4 - StabOx E-Clay – Batch Test Results - BTEX Chemical Oxidation (mg/L)

BTEX		Initial Conc.	Persulphate StabOx E-Clay		Permanganate StabOx E-Clay
			P40 Equil. Conc.	'Activated' P40 + $FeSO_4$ Equil. Conc.	P40 Equil. Conc.
Higher Mix	Benzene	13	6.1	2.9	7.3
	Toluene	12	2.8	0.2	5.8
	Ethylbenzene	40	13	1.7	2.6
	Xylenes	41	6.2	0.27	14
Lower Mix	Benzene	1.6	<0.01	<0.01	0.74
	Toluene	1.5	<0.01	<0.01	0.56
	Ethylbenzene	5.7	0.07	<0.01	0.24
	Xylenes	5.4	0.02	<0.01	1.6

Table 5 - StabOx E-Clay – Batch Test Results - BTEX Chemical Oxidation Treatment Efficiencies

BTEX		Initial Conc.	Persulphate StabOx E-Clay		Permanganate StabOx E-Clay
			P40	'Activated' P40 + FeSO ₄	P40
Higher Mix	Benzene	13	53	78	44
	Toluene	12	77	98	52
	Ethylbenzene	40	68	96	94
	Xylenes	41	85	99	66
Lower Mix	Benzene	1.6	>99	>99	54
	Toluene	1.5	>99	>99	63
	Ethylbenzene	5.7	99	>99	96
	Xylenes	5.4	99	>99	71

The results for the treatment of the higher concentration BTEX mix demonstrated treatment efficacies of **53 to 85%** using the persulphate E-Clay, which increased to **78 to 99%** following activation of the clay with ferrous sulphate. For the permanganate E-Clay treatment efficacies of **44 to 94%** were achieved. Lowest efficacies were observed for benzene with highest efficacies observed for xylenes.

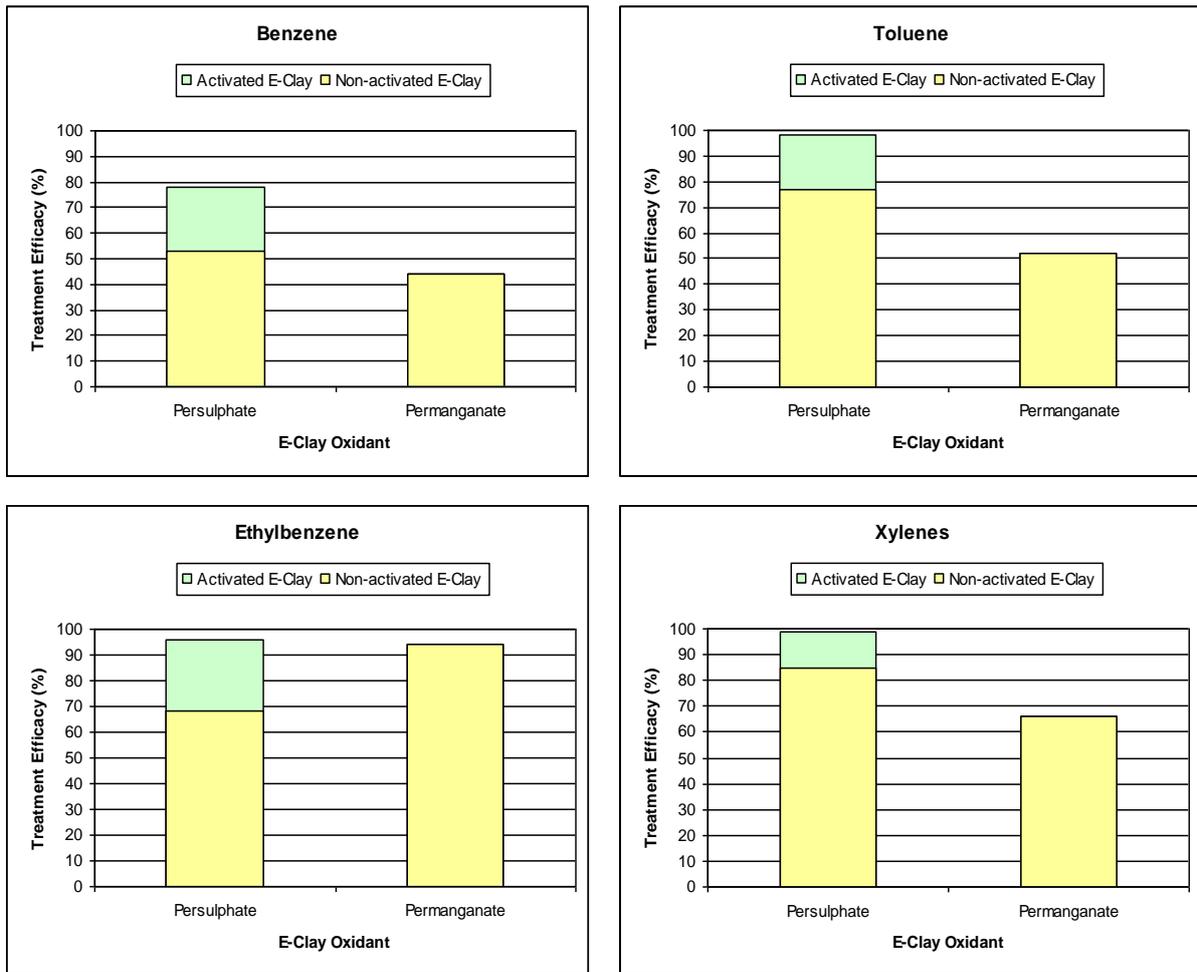
The results for the treatment of the lower concentration BTEX mix showed treatment efficacies of **99%** for persulphate E-Clay both activated and non-activated clays, with treatment efficacies of **54 to 96%** for the permanganate E-Clay. Again lowest efficacies were observed for benzene and highest efficacies were observed for xylenes.

Research carried out elsewhere has proven that ferrous iron [Fe(II)] acts as a catalyst to persulphate oxidation reactions through the formation of sulphate radicals. The activation of the persulphate E-Clay with ferrous sulphate in this instance demonstrated significantly improved treatment performance for BTEX. This is illustrated clearly by Figure 6 which shows treatment efficacy for both clay products for the higher concentration BTEX mix.

The treatment trial for BTEX showed that benzene proved most resistant to chemical oxidation and that the permanganate E-Clay performed worst for benzene, achieving only 44% treatment efficiency. Traditionally permanganate would be expected to show low treatment performance for benzene with other oxidants, such as Fenton's Reagent, preferred for this hydrocarbon (see Table 1 above). The persulphate E-Clay performed better achieving 78% treatment efficiency for benzene once activated with ferrous sulphate. Although not demonstrated by this trial the StabOx E-Clay technology does have capability for the treatment of oxidant resistant hydrocarbons such as benzene by combining chemical stabilisation to the treatment process using an inorgano-organo StabOx E-Clay.

The treatment efficiencies for BTEX are shown diagrammatically in Figure 7 below.

Figure 7 - StabOx E-Clay – Batch Test Results - BTEX Chemical Oxidation Treatment Efficiencies



Chemical Oxidation of Diesel Fuel

The results for the treatment of a diesel fuel hydrocarbon mixture with the persulphate and permanganate StabOx E-Clays are given in Table 6 below. The table provides the equilibrium solution data for the chemical oxidation of the batch test mixes. The initial (untreated) concentration of diesel fuel used for the trial is also given. The data is presented as diesel range organics (DRO) and represents the diesel fuel expressed as carbon banding ranging from C10 to C40 carbon chain lengths speciated into C10 to C20 and C20 to C40 fragments.

Table 6 - StabOx E-Clay – Batch Test Results – Diesel - Chemical Oxidation (mg/L)

		Persulphate StabOx E-Clay		Permanganate StabOx E-Clay
DRO	Initial Conc.	P40 Equil. Conc.	'Activated' P40 + FeSO ₄ Equil. Conc.	P40 Equil. Conc.
C10-C20	26	<0.1	<0.1	<0.1
C20-C40	24	<0.1	<0.1	<0.1
DRO Total (C10 to C40)	50	<0.1	<0.1	<0.1

The results show that both the persulphate E-Clay and the permanganate E-Clay were successful in treating diesel fuel by chemical oxidation. Total DRO concentrations (C10 to C40) were reduced from 50mg/L to less than detection level (<0.1mg/L) for each batch test. This corresponds to a treatment efficacy of >99.8% for each E-Clay formulation tested. A useful point of note is that the persulphate and permanganate E-Clays achieved treatment by direct oxidation of the diesel fuel by the anionic oxidant species (S₂O₈²⁻ & MnO₄⁻) without the need for free radical oxidation by the activated persulphate E-Clay. This fits well with traditional oxidation technology as both persulphate and permanganate oxidants would be expected to adequately deal with diesel range hydrocarbons fairly readily.

5.2.2 Chlorinated Hydrocarbons

Chemical Oxidation of Chlorinated / Substituted Phenols

To demonstrate treatment of chlorinated phenols such as chlorophenol, dichlorophenol and pentachlorophenol three laboratory prepared solutions of mixed substituted phenols were used in the treatment trial. The phenol mixtures were prepared by quantitatively adding equal amounts of each substituted phenol according to the concentrations listed below to give total phenol mixtures of concentrations 10mg/L, 1mg/L and 0.1mg/L (*N.B.* analytical grade phenol reagents were used to ensure purity of each phenol compound). The respective phenol mixes are shown in Table 7 below.

Table 7 – Phenol Mixes

Substituted Phenol	Phenol Mix 10 (mg/L)	Phenol Mix 1 (mg/L)	Phenol Mix 0.1 (mg/L)
Phenol	1.11	0.11	0.011
2-chlorophenol	1.11	0.11	0.011
2-nitrophenol	1.11	0.11	0.011
2,4-dimethylphenol	1.11	0.11	0.011
2,4-dichlorophenol	1.11	0.11	0.011
4-chloro-3-methylphenol	1.11	0.11	0.011
2,4,6-trichlorophenol	1.11	0.11	0.011
4-nitrophenol	1.11	0.11	0.011
Pentachlorophenol	1.11	0.11	0.011
Total Phenol	10	1	0.1

The results for the batch test treatment of the mixed phenol solutions are provided in Tables 8 and 9 below. Table 8 provides equilibrium solution data for the treated mixes and Table 9 lists treatment efficacies as a percentage. For simplification the equilibrium solution data is presented as concentrations of total phenol rather than as speciated concentrations for each phenol compound as used to prepare the test mixtures.

Table 8 - StabOx E-Clay – Batch Test Results – Chlorophenol - Chemical Oxidation (mg/L)

Total Chlorophenol Initial Conc.	Persulphate StabOx E-Clay		Permanganate StabOx E-Clay
	P40 Equil. Conc.	'Activated' P40 + FeSO ₄ Equil. Conc.	P40 Equil. Conc.
0.1	<0.01	<0.01	<0.01
1	0.43	0.61	<0.01
10	8.5	3.9	<0.01

Table 9 - StabOx E-Clay – Batch Test Results – Chlorophenol Chemical Oxidation Treatment Efficiencies (%)

Total Phenol Initial Conc.	Persulphate StabOx E-Clay		Permanganate StabOx E-Clay
	P40	'Activated' P40 + FeSO ₄	P40
0.1	>90	>90	>90
1	57	39	>99
10	15	61	>99.9

The results for the treatment of the mixed phenol solutions demonstrated significant difference in performance between the persulphate E-Clay and the permanganate E-Clay.

For example, the persulphate E-Clay only achieved full oxidation of the 0.1mg/L phenol mixture reaching the <0.01mg/L limit of detection for total phenol and achieving >90% treatment efficiency. However, for the 1 and 10mg/L phenol mixes total oxidation of phenols was not achieved by the persulphate E-Clays. For example, for the 1mg/L phenol mixture 57% treatment efficacy was observed for the non-activated E-Clay with in fact a reduction in efficacy observed for the activated E-Clay with 39% efficacy achieved. For the 10mg/L phenol mixture the persulphate E-Clay only achieved 15% treatment efficacy for the non-activated E-Clay with improvement observed for the activated E-Clay with 61% efficacy achieved.

The permanganate StabOx E-Clay showed much improved treatment performance compared to the persulphate clays with the permanganate E-Clay completely oxidising the three phenol solutions (0.1, 1 & 10mg/L) to less than detection limit with >90% treatment efficacy.

The treatment results for mixed phenols demonstrated that complete chemical oxidation of chlorinated phenols was possible by direct oxidation with the permanganate StabOx E-Clay product. Free radical oxidation of phenols by the persulphate E-Clay showed promise however, the permanganate E-Clay would be the product of choice for the chemical oxidation of chlorinated phenols.

Chemical Oxidation of Trichloroethylene (TCE)

To demonstrate treatment of chlorinated alkenes with the StabOx E-Clay products the chlorinated hydrocarbon TCE was chosen. Two laboratory prepared solutions of concentration 50mg/L and 5mg/L TCE were used for the treatment trial.

The results for the treatment of TCE with the persulphate and permanganate StabOx E-Clay products are given in Table 9 below. The table provides the equilibrium solution data for the treated batch test mixes.

Table 10 - StabOx E-Clay – Batch Test Results – TCE - Chemical Oxidation (mg/L)

	Initial Conc.	Persulphate StabOx E-Clay		Permanganate StabOx E-Clay
		P40 Equil. Conc.	'Activated' P40 + FeSO ₄ Equil. Conc.	P40 Equil. Conc.
TCE	50	<0.1	<0.1	<0.1
TCE	5	<0.1	<0.1	<0.1

The results show that all StabOx E-Clay formulations tested were successful in treating TCE by chemical oxidation, with TCE concentrations reduced to less than detection level (<0.1mg/L) for each test mix. This corresponds to a treatment efficacy of >99% for each E-Clay formulation tested. The treatment results demonstrated that complete chemical oxidation of TCE was possible by direct oxidation with both the permanganate and persulphate StabOx E-Clay products.

The permanganate ion is an electrophile and therefore is strongly attracted to the electrons in carbon-carbon double bonds found in chlorinated alkenes such as TCE. By using the electron density from the double bonds the permanganate ion is able to form an unstable intermediate hypomanganate ester. This intermediate product further reacts by a number of mechanisms such as hydroxylation, hydrolysis or cleavage. Under most naturally occurring environmental conditions the carbon-carbon double bond of alkenes is broken spontaneously and the unstable intermediates are converted to carbon dioxide by further oxidation by permanganate. The permanganate StabOx E-Clay would therefore be the product of choice for the treatment of chlorinated alkenes such as TCE. However, the results presented here suggest that the persulphate product both activated and non-activated would also be suitable for use widening the scope of treatment options available for treatment of chlorinated alkenes using StabOx E-Clays.

6.0 Conclusions

Chemical oxidation provides an effective treatment for oxidisable organic pollutants. The process rapidly destroys / degrades organic contaminants leaving significantly less harmful breakdown products. A variety of oxidants such as hydrogen peroxide, percarbonate, permanganate, persulphate and ozone have been traditionally used for the chemical oxidation of contaminated soils and groundwater. Applied *in-situ* the treatment process has given significant contaminant mass reductions that have been observed at many sites.

A range of StabOx E-Clay products have been developed for application to chemical oxidation treatment processes using persulphate and permanganate oxidant species. In addition the StabOx process can also incorporate the use of hydrogen peroxide, preferably as a two stage process (chemically oxidising previously immobilised organic pollutants). The StabOx E-Clays were developed from existing E-Clay technology offering multi purpose treatment performance that can be applied for the treatment of organic contaminants by chemical oxidation combined with chemical stabilisation (immobilisation). The StabOx E-Clays also contain residual capacity for treatment of inorganic pollutants such as heavy metals using cation-exchange processes.

StabOx E-Clays have been shown to have capability to chemically oxidise non-chlorinated and chlorinated hydrocarbon pollutants including phenols, BTEX, diesel fuel and chlorinated alkenes (TCE) with up to 99% treatment efficiencies achieved for all contaminants tested.

The StabOx E-Clay technology can be applied in solid form enabling greater control over oxidant-contaminant matrix interactions reducing the requirement for the use of excess chemicals in the environment. The StabOx E-Clay technology can be applied for the treatment of both soils and groundwaters using the Envirotreat[®] Process which has been successfully utilised 150 projects within the UK. The development of a StabOx product range means that the E-Clay technology can be easily tailored according to pollutant levels on a site-specific basis and thus offer a cost-effective solution for the treatment of contaminated soils and groundwaters.