CHEMICAL FIXATION OF INORGANICS USING MODIFIED CLAYS

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Abstract

The use of modified clays in the treatment of both inorganic and organic pollutants is a developing technology with the potential for wide application. Organophilic clays have been successfully utilised in the treatment of organic wastes and have recently been used in a contaminated land remediation project in the UK [1]. Modified inorganoclays have now been developed which can effectively treat both cationic and anionic inorganic species. This paper gives a brief synopsis of the modified clay technology with particular emphasis on the treatment of toxic heavy metals in both stabilisation/solidification processes and active containment systems.

Background to Modified Clay Technology

The treatment technology is essentially an advanced immobilisation (chemical fixation) process targeted at soils contaminated with both organic and inorganic/heavy metal pollutants. The process is based on the use of modified pillared and non-pillared smectite clays which incorporate reactive species. Once intercalated, the reactive properties of the clay and the presence of reactive species will ensure that the waste contaminant is effectively immobilised within the substrate material. The non-pillared clays can be used as specialist additives in stabilisation processes. Pillared clays have particular application in active containment systems. The pillaring effect facilitates the passage of contaminated water through the clay bringing the pollutants into direct contact with intercalated reactive species and enabling the reactive clays to be used in permeable reactive walls/reactive gate systems.

Smectite clay minerals possess a combination of cation exchange, intercalation and swelling properties which make them unique. The diagrammatic structure of smectite clay is as shown in Figure 1.

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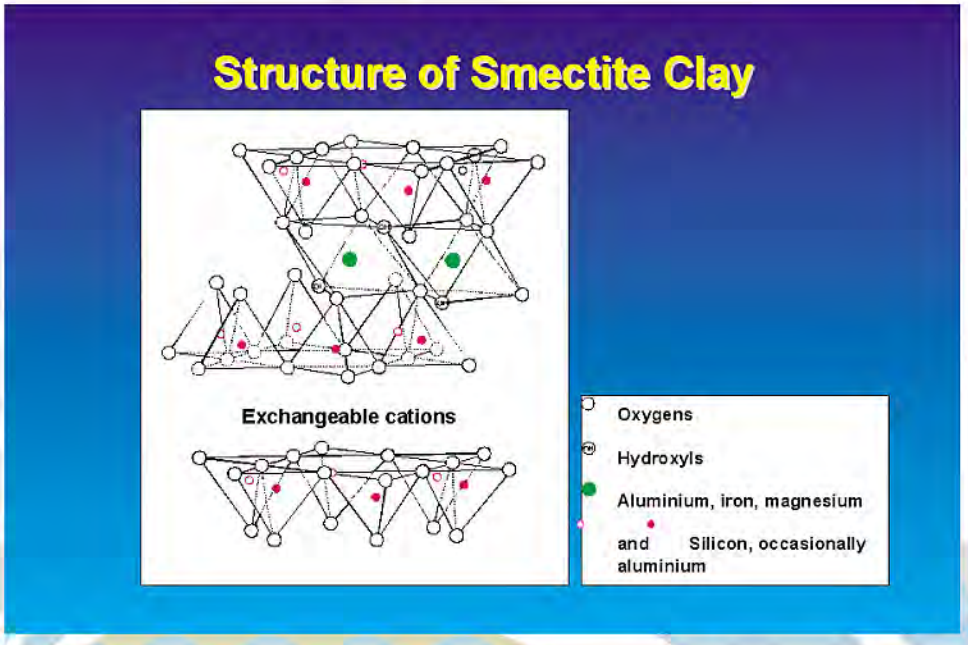
Figure 1. Structure of Smectite Clay.



The smectite clay structure is negatively charged due to isomorphic substitution of higher valency cations (typically Si^{4+}) with lower valency cations (e.g. Al^{3+} in montmorillonite; Mg^{2+} in saponite). Electroneutrality is maintained in nature by the intercalation of cations (typically Na^{+} or Ca^{2+}); these cations are readily exchangeable and can be displaced by cations or cationic groups with a stronger charge affinity for the negative clay structure. Smectite clays can be modified with selected intercalatants to produce "organoclays" and "inorganoclays"; these modified clays are commonly utilised in the paint/oil and catalysis industries respectively.

Pillared clays are commonly used in the catalysis industry. The intercalated "pillars" act as molecular props creating a two-dimensional porous interlayer structure. These pillars are typically formed from intercalation of hydroxy-aluminium polymers (predominantly $Al_{13}O_4(OH_{24}).12H_2O^{7+}$).

A new range of modified clays has been developed for environmental application [2]. These modified clays exhibit multireactive properties and can be used for the treatment of both organic and inorganic pollutants.

Modified inorganoclays have been developed which have the capability to react with both cationic and anionic metal species. Conventional smectite clays (*e.g.* bentonite) exhibit cation exchange properties in

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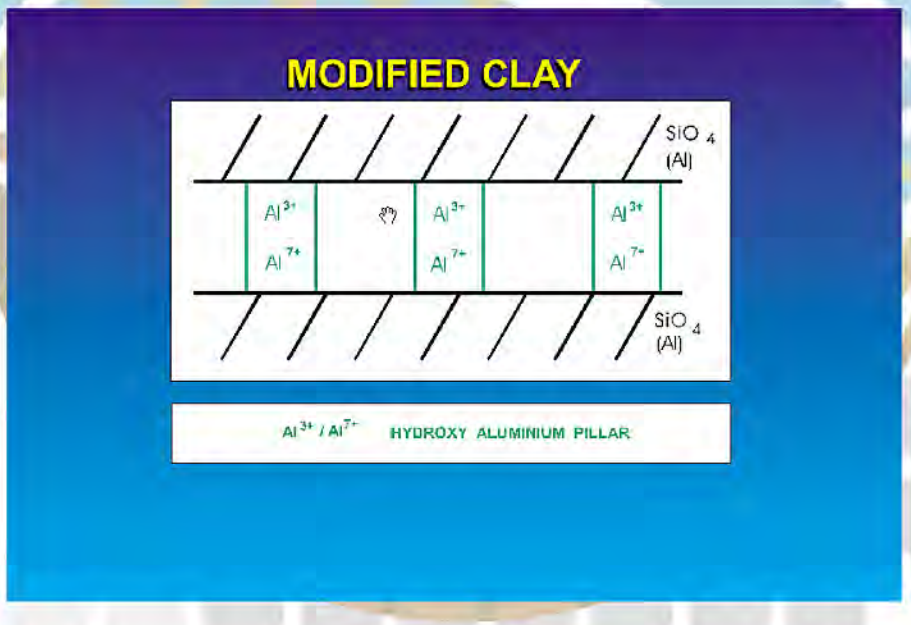
similar fashion to zeolites which can be utilised in the treatment of cationic species (e.g. $Cu^{+/2+}$, Ni^{2+}, Zn^{2+}, NH_4^+). They are not however suitable for the treatment of problematic anionic and anionic complexed species, in particular Chromates / Dichromates, Arsenates and Ferro / Ferricyanides. The inorganoclays can either be fully modified or only partially modified depending on the application; the full modification process produces an inorganoclay with the capability of treating primarily anionic species whereas partial modification produces an inorganoclay with the capability of treating higher proportions of cationic species in addition to anions (this is particularly advantageous when treating wastes containing cationic and anionic species which commonly occur together e.g. Cr^{3+} and Cr^{6+}).

The structure of a fully modified inorganoclay is as shown in Figure 2. The calcium/sodium ions are completely replaced (*i.e.* 100% exchanged) by hydroxy-aluminium cations. This form of inorganoclay has been demonstrated as being effective in the treatment of cationic species (*e.g.* Cd^{2+} and Cu^{2+}) in addition to anionic species [3].

Figure 2. Fully Modified Inorganoclay.



The structure of a partially modified inorganoclay is as shown in Figure 3. In this case the calcium / sodium ions are exchanged to varying degrees depending on the application (*i.e.*, 0 - 100%). In a situation where cationic species predominate, the degree of intercalation will be relatively low and *vice versa*.

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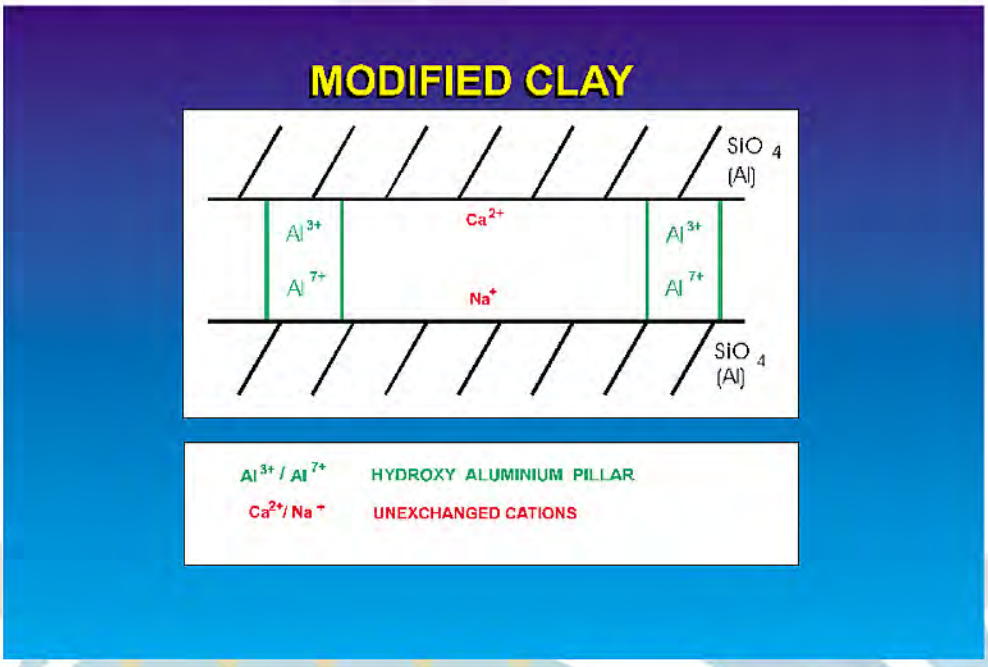
Figure 3. Partially Modified Inorganoclay.



The potential reactivity of a modified inorganoclay is as shown in Figure 4. In the majority of cases involving contaminated land remediation, there will be a requirement to address a broad range of contamination problems. Figure 4 focuses on toxic heavy metals which are likely to be present in both cationic and anionic forms. Toxic heavy metals would occupy the interlamellar spaces (predominantly cationic species e.g., Cu^{+} and Ni^{2+}) and would be bound to the hydroxy-aluminium pillars (predominantly anionic species e.g., Cr^{6+} in the form of CrO_4^{2-} / $Cr_2O_7^{2-}$).

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Figure 4. Potential Reactivity of Modified Inorganoclay.

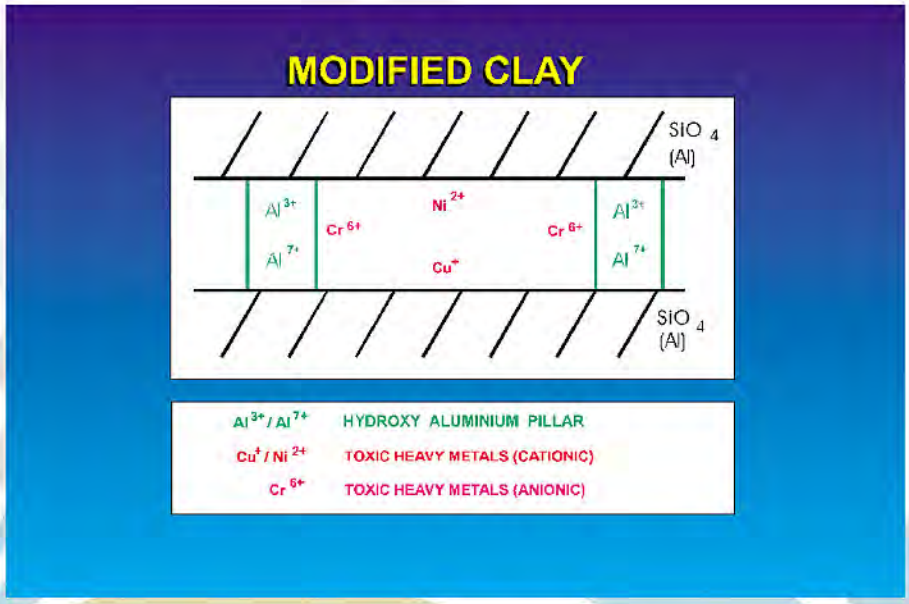
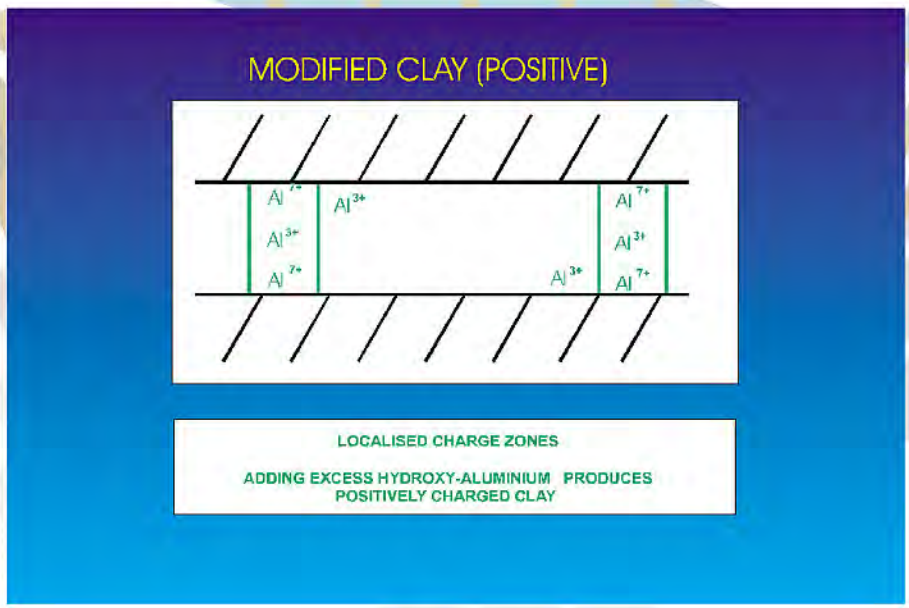


Figure 5. Modified Inorganoclay (Positive).



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Another form of modified inorganoclay is as shown in Figure 5. This form of clay is engineered to be positive by intercalating hydroxy-aluminium cations to excess. This clay is particularly suited to the treatment of soils contaminated with pure anionic species *e.g.*, ferro / ferri cyanides.

Modified inorganoclays have been evaluated in the treatment of soils contaminated with chromium wastes. The contamination comprised of both trivalent and hexavalent chromium however the prime focus was on hexavalent chromium due to perceived problems with treatability.

Batch treatment trials were carried out to establish the effectiveness of the modified clays in direct comparison to other potential absorbents and reactive media. Comparative data for an Envirotreat modified inorganoclay "E-Clay" and unmodified bentonite is as shown in Figure 6.

Figure 6. Comparative Absorption Data for Modified and Non-Modified Clays.

HEXAVALENT CHROMIUM
Batch Test Results
Chromium Envirotreat Clay

Initial Concentration		pH		Concent. at equilibrium mg / L	X / m (mg / g)		Q' (meq / 100g)	
Theoretic mg / L	Measured mg / L	Initial	at equilib.		Theoretic	Measured	Theoretic	Measured
100	101.0	7.3	6.7	2	3.92	3.96	45	46
10	10.0	8.0	6.8	0.02	0.40	0.40	5	5
1	1.0	9.2	7.1	0.02	0.04	0.04	0	0
Chromium Unmodified Bentonite								
100	101.0	7.3	8.9	101	-0.04	0.00	0	0
10	10.0	8.0	9.0	10	0.00	0.00	0	0
1	1.0	9.2	8.9	1	0.00	0.00	0	0

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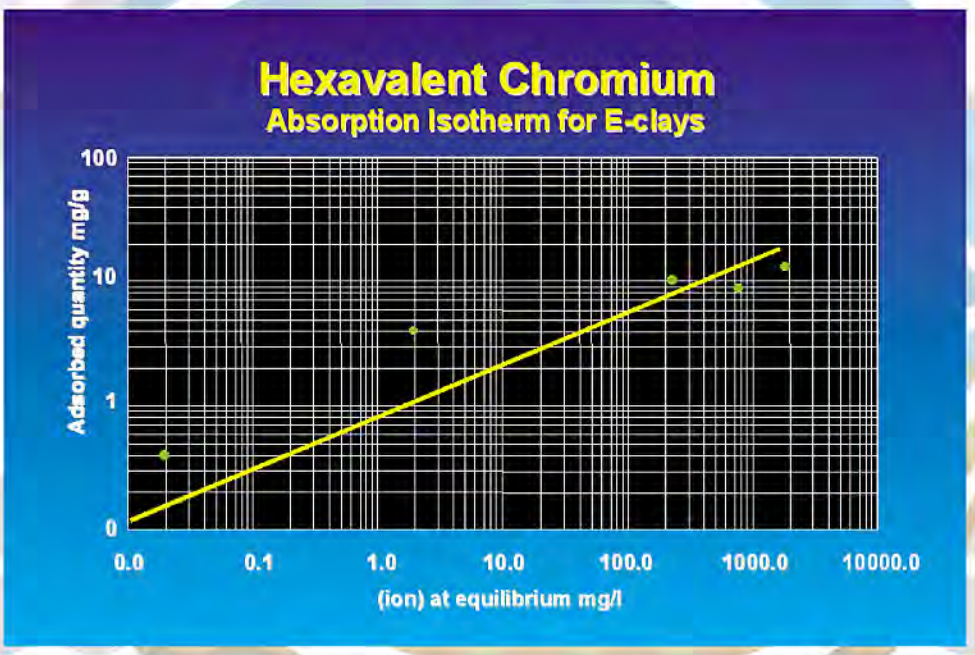
These batch trials were carried out using a solution of Sodium Chromate with concentrations varying between 1 and 100 mg/L of Cr^{6+}. The clay mass was fixed at 2.5g in each case. The clay material was added to 100mls of solution and agitated for 16 hours. The solution was then analysed for residual Cr^{6+}.

The results clearly demonstrate that the modified clay is an effective sorbent for Cr^{6+} whereas the unmodified bentonite is totally ineffective. The results for the modified clay were plotted to determine the absorption characteristics; straight-line absorption isotherm graphs were obtained as shown in Figure 7. N.B. absorption data for higher concentrations of chromate solution is incorporated into these graphs.

Figure 7. Absorption Isotherm Graph for Hexavalent Chromium using Envirotreat Modified Clay (E-Clay).



Further tests were carried out to compare the absorption capabilities of E-Clay with a range of potential sorbents. The results obtained were summarised as isotherm parameters using the Freundlich Model. It was demonstrated that hexavalent chromium is not absorbed by conventional bentonites (which are inappropriate for anionic treatment processes); it was further demonstrated that the best treatment media was the E-Clay as formulated by Envirotreat Limited, as indicated by the highest K value. The results obtained are as shown in Table 1.

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In summary, modified inorganoclays are effective in treating both cationic and anionic species and can be applied to a broad range of contamination problems. They can be used in conjunction with organophilic clays in the treatment of soils contaminated with a mixture of organic and inorganic pollutants. Two specific applications of the technology have been identified in the treatment of contaminated land *viz.* as an additive in stabilisation / solidification processes and as a treatment material in active containment systems. Modified pillared clays have particular relevance to reactive gate technologies which primarily address ground water contamination problems.

Table 1. Comparative Absorption Capabilities.

COMPARATIVE ABSORPTION CAPABILITIES

MEDIA	K (L/g)	1/n
BENTONITE 1		0.00
BENTONITE 2		0.00
E-CLAY	1.76E + 00	0.40
FLYASH	2.04E - 02	0.98
SLAG	3.70E - 11	3.14
BENTONITE 3	4.02E - 02	0.89
BENTONITE 4	4.58E - 02	0.92
ACTIVATED CARBON	5.25E - 02	0.85
SAND	2.38E - 02	1.04

Application in Stabilisation/Solidification Processes

Stabilisation and solidification processes have been applied to the treatment of contaminated soils and hazardous wastes for several years. The United States Environmental Protection Agency (USEPA) regards stabilisation/solidification (S/S) as an established treatment technology; the USEPA Superfund Programme Records of Decision show that 29% of remediation projects carried out during the period 1982-1994 incorporated S/S as part of the selected treatment process making S/S the most frequently selected technology. S/S technologies are not commonly used at present for the remediation of contaminated land in the UK but have found applications in the treatment of hazardous wastes, particularly as a pretreatment process prior to landfilling.

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The term solidification is used to describe processes which aim to improve the physical properties of the treated soil or hazardous waste whereas the term stabilisation (chemical fixation) refers to processes which aim to chemically immobilise the waste constituents within the treatment media. In most cases, effective treatment can only be carried out by using a combination of these processes, for example, using specialist additives with conventional cementitious materials.

Stabilisation processes have been predominantly applied to the treatment of soils contaminated with toxic heavy metals. In most cases the process involves the use of cementitious/pozzolanic materials (Portland Cement and cement substitutes). Whilst the chemistry of the process is almost certainly complex (particularly during the curing/solidification process) the prime stabilisation objective is to reduce the solubility of the heavy metal species to a minimum by aiming for an optimum pH of typically 8-10; this process is analogous to the treatment of industrial effluents containing heavy metals where the metal is precipitated out of solution by the addition of alkaline reagents.

Once converted into an insoluble form, the heavy metal species can be incorporated into the cementitious / pozzolanic treatment media and be subsequently encapsulated as part of the solidification process; this process is primarily physical but may well involve further chemical interaction between the intermediates in the cement curing process and the heavy metal species.

Whilst the treatment of industrial effluents containing inorganic / heavy metal species is relatively easy to control and implement (often by a staged approach), it is considerably more difficult to treat soils contaminated with a "cocktail" of contaminants which can include both inorganic and organic pollutants (or even a combination of both *e.g.* organo-metallic compounds). The treatment of heavy metals can pose significant problems for stabilisation technologies. Individual heavy metals and not all metals are in a form that is readily amenable to treatment by this method (*e.g.* Cr^{6+}). It is usually impracticable and uneconomic to carry out a series of treatment processes to achieve the optimum for each individual species. It is also difficult to accurately control pH by the addition of cementitious materials. In summary, conventional S/S processes have distinct limitations in the treatment of complex contamination problems and are inappropriate for the treatment of anionic and complexed metal species without the addition of special additives.

By incorporating modified inorganoclays, the problematical heavy metals can be treated as part of the overall S/S process. The inorganoclays form part of the cementitious matrix into which the anionic species are consolidated. The resulting stabilised mass can then be allowed to cure and tested using conventional evaluation techniques such as leachability etc. Samples evaluated during an *in situ*

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treatment trial resulted in an empirical remediation factor of 5.3 x 10^3 (*i.e.*, average total soil concentration 53mg/Kg; treated leachate value using Toxic Characteristic Leaching Procedure 0.01mg/L); the leachability value was a factor of nominally 10^2 lower than the optimum solubility value for trivalent chromium and also reflected encapsulation of hexavalent chromium using the S/S process incorporating modified inorganoclays[2].

Application in Active Containment / Reactive Gate Systems

The potential use of modified inorganoclays in active containment systems is a developing technology. The prime objective would be to treat mobile contaminants within a ground water plume using either peripheral active containment systems or reactive gate mechanisms.

The pillaring effect provides a means for ground water to pass through the treatment media. The hydroxy-aluminium pillars are reactive and can treat both cationic and anionic species; pillared clays can be produced as either fully modified or partially modified as described in the modified clay technology overview.

Treatment of hexavalent chromium polluted ground water using modified E-Clays has been proposed for applications where stabilisation / solidification techniques are either inappropriate and / or non cost-effective or alternatively where practical and logistical considerations render other techniques inappropriate. Active containment systems are particularly suitable for treatment of contaminated sites which are currently used for industrial production purposes or for existing residential use.

The two potential applications of the technology are as shown in Figures 8 and 9 respectively. A peripheral active containment system as shown in Figure 8 can be varied to suit the application and can in fact comprise of a mixture of passive (very low permeability) barriers and active containment walls. The passive barriers would be constructed with unmodified clays such as bentonite whereas the active walls would be constructed using modified clays. The reactive gate approach would involve passive barriers or engineered cut-off walls around the majority of the site with a gate system at an appropriate point; the engineered gate system could then incorporate modified inorganoclays.

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Figure 8. Peripheral Active Containment System.

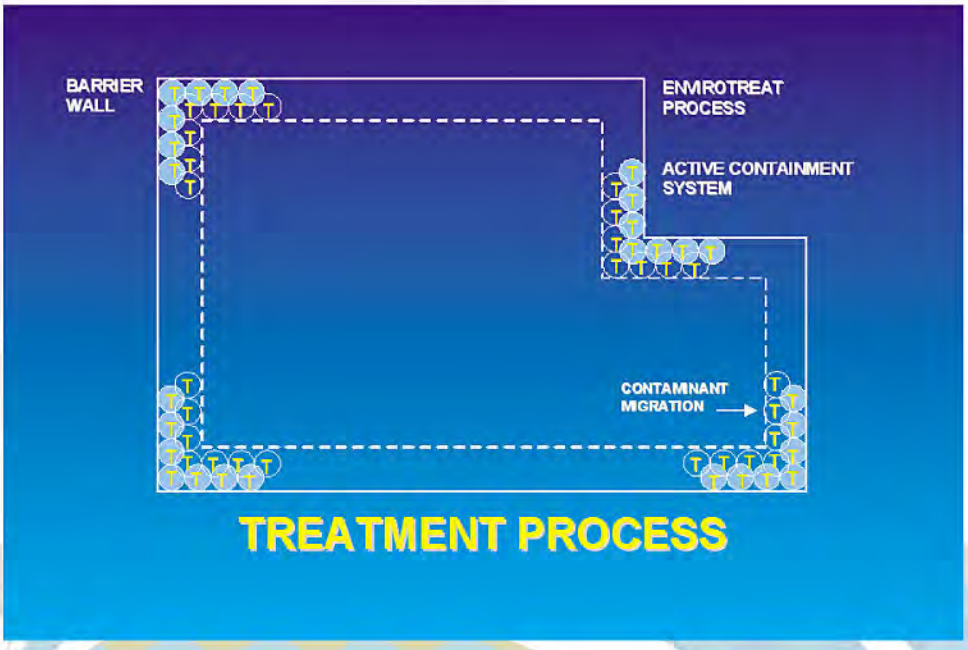
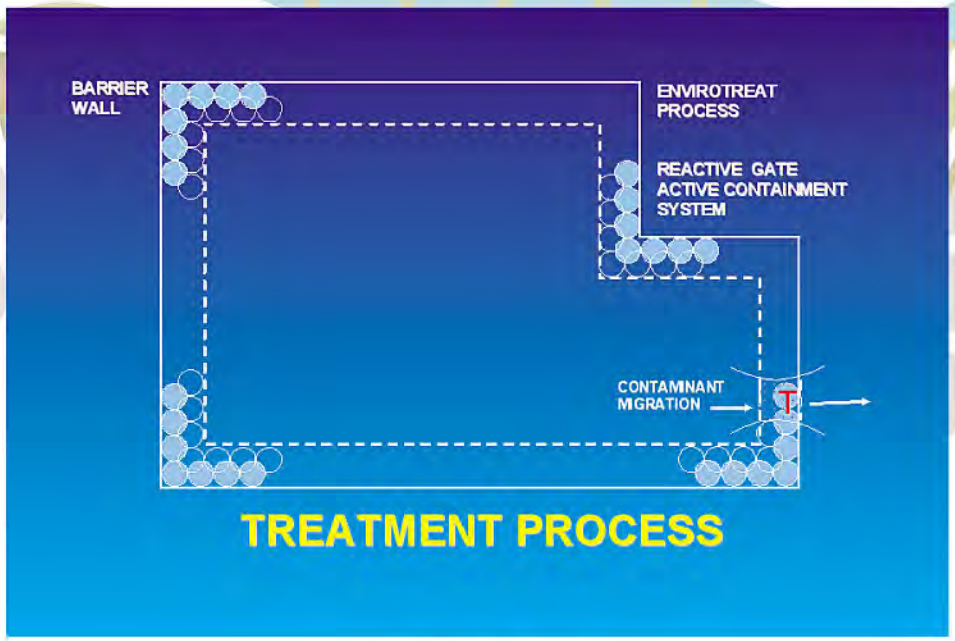


Figure 9. Reactive Gate Active Containment System.



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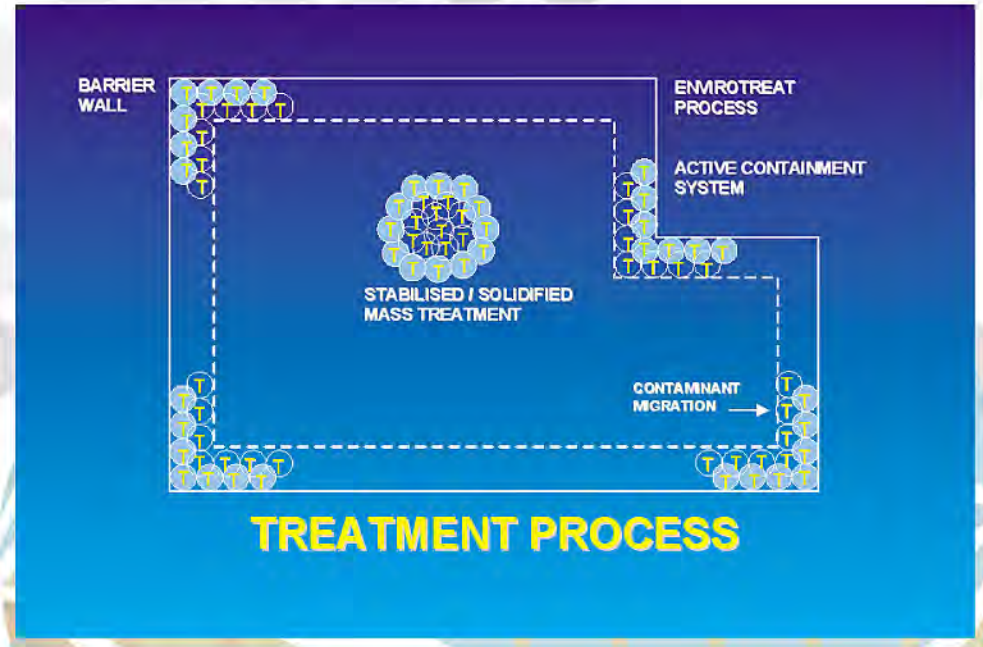
The stabilisation / solidification process can be effectively combined with active containment technology to treat a contaminated site as a whole. This combined approach has been successfully applied to a contaminated site in the UK [1]. A typical approach is as shown in Figure 10.

Figure 10. Combined Stabilisation/Solidification and Active Containment.



Conclusions

The application of modified pillared and non-pillared inorganoclays to the remediation of contaminated sites is a developing technology with significant potential. The technology is versatile and can be applied to a broad range of contamination problems. Recent development work with inorganic wastes containing cationic and anionic species has demonstrated the potential of this technology for treating problematical inorganic species which are difficult to treat by other means.

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References

1. Cleaning up on site. Article in *Construction News No. 6532.* September 1997.

2. McLeod, N. (1996). *Chemical Fixation of Soils Contaminated with Organic Chemicals.* Final Report for NATO / CCMS Pilot Study, Phase II. Presentation in Denver, Colorado.

3. Furrer, G., Lothenbach, B., Scharli, H. & Ludwig, C. (1994). Interactions Between Polynuclear Aluminium Compounds and Heavy Metal Ions. *J. Ecol. Chem. No 3,* p. 303-312

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