

Organo-Clay Reactive Barriers in Contaminated Site Remediation

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Summary: Increased awareness of the total environmental impact and economics of many common site remediation strategies has led to interest in natural attenuation. Natural attenuation is any process that reduces the concentration or toxicity of environmental contaminants, without the aid of human intervention. The most commonly cited reasons for not utilising natural attenuation are that the process takes longer than the project timeframe and there is no guarantee that contaminants will not migrate into the air or groundwater. A barrier system could be used to allow development to continue and provide the time required for the processes to run their course. It would also provide a guarantee against further migration. Conventional barrier systems rely on minimising advective flow, however contaminants can still travel quite effectively by diffusion. Reactive barrier systems utilise contaminant reactions to reduce contaminant transport. This paper outlines some of the research being conducted into natural and organically modified clay barriers for the immobilisation of environmental contaminants.

1 INTRODUCTION

Contaminated site management in Australia is currently in a state of change. New technologies are continually being presented as the waste management cure all. However, many of these strategies require high energy input or involve exposing the contaminants. In industrial production, increased emphasis is being placed on total environmental impact. If a life cycle analysis is performed on many contaminated site remediation projects, the results indicate that the least environmental impact is achieved by not doing anything [1]. This has led to increased interest in natural attenuation.

Natural attenuation is any process that reduces the concentration or toxicity of environmental contaminants, without the aid of human intervention. Examples of such processes are biodegradation of organic compounds and adsorption of heavy metals onto soil particles. Both of these processes have been proven to reduce the concentration of certain contaminants [2]. However, these processes do have limitations. Bioremediation takes time to be effective and high concentrations of organic compounds can kill the bacteria that are responsible for biodegrading lesser concentrations. Adsorption of inorganic ions to soil particles is governed by the concentrations of ions available and is limited by a maximum capacity. These limitations make it hard to confidently rely on these processes to manage contaminant concentrations and movement.

Currently natural attenuation is only utilised in conjunction with extensive monitoring programs. A barrier system could be used to isolate the site to ensure contaminants are unable to pass across site boundaries or enter environmentally sensitive systems, such as groundwater or surface waters, then the natural attenuation processes could be left to manage the contaminants within the isolated zone. Some monitoring would still be required, but on a much lesser scale.

The commonly used barriers to contaminant migration focus on minimising advective and/or diffusive transport. To achieve sufficiently low contaminant movement this approach often requires the placement of thick compacted clay liners or high density polymer materials. Both of these options are expensive, time consuming and interfere with the natural hydraulic movement across the site. Reactive barriers increase retardation of the contaminants. By incorporating materials that adsorb contaminants in a porous matrix, contaminant transport can be reduced without affecting hydraulic flow.

The same principle can be used in solid waste management. The adsorbent materials can be incorporated in a low permeability material to minimise hydraulic flow and contaminant movement. Layers can be used as part of a landfill liner system and are commonly referred to as attenuating layers.

2 REACTIVE BARRIER TECHNOLOGIES

Contaminant transport comprises of three components; advection, diffusion and reaction [3]. Contaminant mobility can be minimised by minimising advection and diffusion and/or maximising reaction.

Advection is governed by hydraulic gradient and hydraulic conductivity. The hydraulic gradient is a characteristic of the given site conditions and can not be varied greatly. Low hydraulic conductivity is the major selection criterion for barriers. Compaction is used to minimise the hydraulic conductivity of the material chosen. Advection is the component of transport most commonly investigated and is generally minimised as much as practicable. Diffusion is governed by the diffusion coefficient of the particular contaminant and porosity of the material. The diffusion coefficient is constant for a given compound at a constant temperature and pressure. Porosity for a particular material is generally minimised, along with hydraulic conductivity, by

compaction. Reaction can describe many different processes, none of which are commonly used in barriers or liners.

Different contaminant groups can be immobilised by different techniques. Therefore, to utilise reactive barriers a good understanding of the contaminants present is required. Some of the mechanisms which can be utilised are briefly described below [4], [5].

2.1 pH Control

pH control is the most common mechanism used for metal fixation. Most techniques employing pH control, raise the pH to within the range where metal hydroxides have the lowest solubility by using a material which has a high pH and high acid buffer capacity. That is, addition of acid does not necessarily lower the pH of the material. This results in precipitation of the metals. Figure 1. shows the solubilities of metal hydroxides as a function of pH.

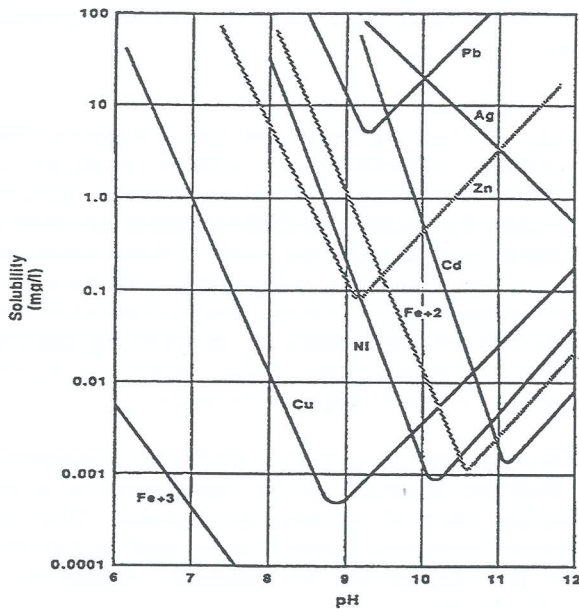


Figure 1: Solubility of metal hydroxides as a function of pH. [4]

As can be seen from Figure 1, there is no pH range that is ideal for minimising the solubility of all metals. However, pH above 8 is generally considered to be beneficial. A good understanding of the metals of concern and the species present in the waste is necessary for the successful employment of this mechanism.

2.2 Oxidation or Reduction

Oxidation or reduction can change the valence of some metals such as chromium and arsenic. These changes in valence can result in a significant change in mobility. The redox potential can be used to identify if oxidation or reduction is likely to occur. Little work has been done to provide an estimate of the mobility of metals based on the redox potential.

2.3 Adsorption of Contaminants to Clay Minerals

Clay minerals consist of various arrangements of tetrahedral and octahedral silicate sheets. This construction results in

clays having a large specific surface area. Substitution of atoms in the sheet structure results in a net negative charge over the clay surface. This charge is usually balanced in nature by calcium, sodium or magnesium ions. However, these cations are exchangeable and can be replaced by almost any positively charged ion. A schematic of this process is shown in Figure 2. This mechanism can be quite effective for immobilisation of metal ions. The maximum adsorption is limited to the cation exchange capacity of the clay.

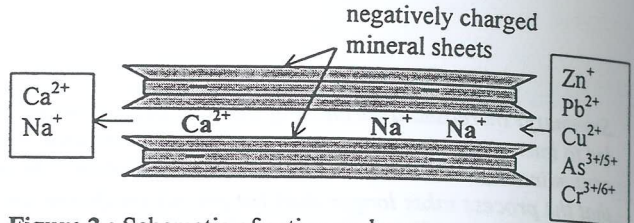


Figure 2 : Schematic of cation exchange.

2.4 Adsorption of contaminants to organically modified clays

By the mechanism described above, organic cations can be bonded to clay mineral surfaces [6]. Organic cations usually consist of a cationic end (often ammonium) and a long organic tail. Adsorption of these cations leads to pillaring of the interlayer spaces in the clay material. That is, the long organic chain keeps the silicate sheets apart. This enables organic compounds to access the interlayer spaces where they can be adsorbed onto the mineral surfaces [7]. In addition, organic compounds are attracted to the organic ends of the cations and form micelles [8]. A schematic of organic compound adsorption is shown in Figure 3. By this process the clay surface is modified from hydrophilic to organophilic. Adsorption on to the mineral surfaces is limited by the physical space available whereas adsorption through organic-organic attraction does not seem to be limited.

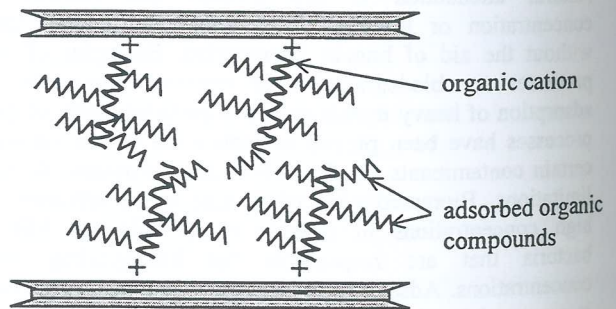


Figure 3 : Schematic of organic compound adsorption to organically modified clay.

Organically modified clays are prepared by adding organic cations, generally quaternary amines, to the natural clay in quantities up to the cation exchange capacity. Organic cations with differing organic groups are used to target different organic contaminants.

3 IMPLEMENTATION OF REACTIVE BARRIERS

There is no single formulation for a reactive barrier, containing natural or organically modified clay, that

effectively immobilises all contaminants. As with compacted clay liners, a thorough investigation is necessary prior to use. Several combinations of clay types and organic modifiers may be trialed using actual contaminated samples or samples prepared to simulate expected conditions. Ionic strength and pH greatly affect the performance of adsorption to natural clays. Therefore, it is vital that expected site conditions are induced during laboratory trials. Laboratory tests can include: batch adsorption tests (see Figure 4), which involve total particle-solution contact and provide an indication of the relative efficiency of adsorption of various contaminants to clays, or column advection-diffusion tests (see Figure 5), which test combination of barrier materials in the condition they will be used and provide an indication of how the barrier material will actually perform.

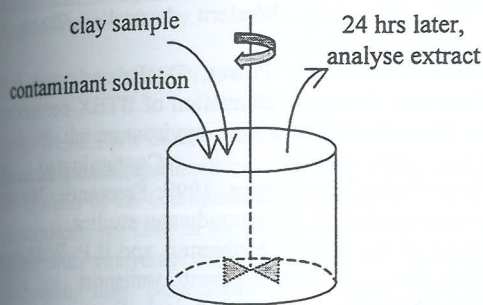


Figure 4: Schematic of batch adsorption test [9].

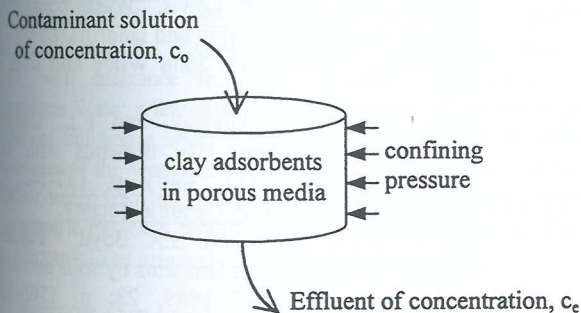


Figure 5: Schematic of column advection-diffusion test.

Since reactive barriers are prepared specifically for site conditions, it is worth investigating the use of natural clay from the site. There are a few preliminary tests that are useful to assess the suitability of clay for contaminant immobilisation. High surface area and cation exchange capacity are desirable characteristics.

4 CURRENT RESEARCH

Research, currently being undertaken at Monash University, is focussing on the retardation of selected metals and organics by three Australian clays; Saponite from Perth, basaltic clay from Melbourne and commercial bentonite from Brisbane.

Tests have been conducted to assess the physical characteristics of the clays. Surface area, cation exchange capacity, particle size distribution and mineralogy were all

investigated. The results of the surface area and cation exchange capacity tests are presented in Table 1.

Table 1 : Clay surface properties.

Clay Type	Surface Area (m ² /g)	Cation Exchange Capacity (meq/100 g)
Saponite	270.4	32.1
Basaltic	252.4	45.3
Bentonite	410.2	63.5

meq = milliequivalents

The surface area and cation exchange capacity results indicated that all three clays had a good potential for use as contaminant adsorbents in a reactive barrier.

Acid buffer capacity has also been investigated. A high acid buffer capacity can be valuable in acidic applications, such as mine tailings dams. Metals can be immobilised by a material with high acid buffering capacity despite being in an acidic environment. However, it must be noted that there is a limit to acid buffering capacity. In long-term projects there is a risk of the pH in the material suddenly dropping and the immobilised metals being released. Results of the acid buffer capacity tests are presented in Figure 6.

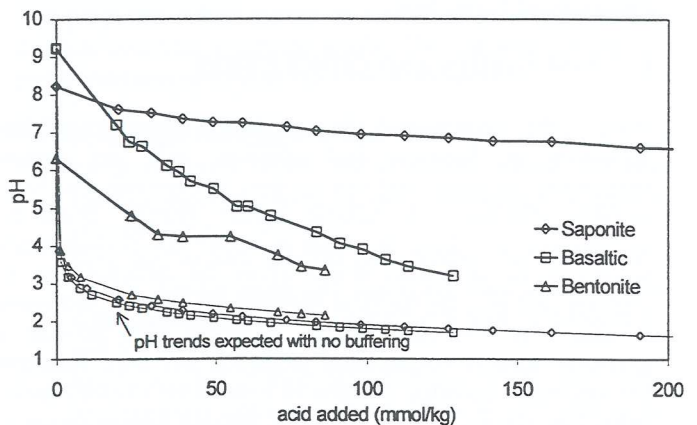


Figure 6: Acid titration curves.

The set of curves that lie between pH of 2 and 3 represent the pH expected if there was no buffering action by the clays. The results of the acid buffering tests show that basaltic clay and bentonite have a low resistance to change in pH, whereas saponite has a very high acid buffering capacity.

Batch adsorption tests have been conducted for adsorption of copper, lead and zinc to the clays. It was expected that the adsorption of metal ions would be limited to a maximum capacity equal to the cation exchange capacity. This was the case for bentonite and basaltic clay. However, saponite achieved adsorption in excess of the estimated cation exchange capacity. There are two potential explanations for this. The estimated cation exchange capacity may be incorrect or there may be other mechanisms acting to increase immobilisation. When the pH of the equilibrium solution and the concentration of metal ions remaining in the solution were plotted together, the curves were very similar. This was not

the case for basaltic clay and bentonite. This leads to the conclusion that the high pH buffer capacity of the saponite increased the immobilisation of metal ions.

The adsorption of organic compounds to natural soil is related to the organic carbon content of the soil and the organic partitioning coefficient of the organic compound of interest [9]. In other words, how much organic material is there in the soil and how strongly are the contaminants attracted to other organic matter. The three clays were analysed for total organic carbon. The basaltic clay and bentonite had very low organic contents, approx. 0.1%, whereas the saponite had a relatively high organic carbon content, approx. 5%. This suggests that the basaltic clay and bentonite would have a very low potential for adsorption of organic compounds in their natural condition. However, by utilising their high cation exchange capacities, through organic modification, it is anticipated that the organic compound adsorption potential of these clays can be greatly increased.

Future testing is planned to focus on the performance of these clays in a matrix of low permeability material, as would be used in an attenuating layer for solid waste management. Flexible wall permeability testing equipment has been modified to facilitate the use of contaminant solutions [10], [11]. It is proposed to correlate the results of this testing with a contaminant transport model that has been developed at the University of Turin, Italy.

5 DISCUSSION AND CONCLUSION

Many of the contaminated site remediation strategies gaining popularity in Australia and overseas, rely on natural attenuation processes that can be time consuming and have variable efficiency. A reliable barrier system could be incorporated into these strategies to isolate the contaminants present at the site. This would allow the development to continue and provide the time required for natural processes to immobilise the contaminants. It would also provide a guarantee against contaminant migration off site. Reactive barriers utilise chemical reaction to immobilise contaminants, rather than relying on flow reduction through minimisation of advective and diffusive transport.

Preliminary tests have shown that three Australian clays have a good potential for use as contaminant adsorbents in reactive barriers. Basaltic clay from Melbourne and commercial bentonite from Brisbane adsorb metal ions through cation exchange. Saponite from Perth adsorbs metal ions in excess of the cation exchange capacity, which indicates a second mechanism. It is considered that this is due to precipitation of metal hydroxides due to the high acid buffer capacity of the saponite.

None of the clays is expected to naturally immobilise organic compounds. However, their high cation exchange capacity can be utilised, through organic modification, to create organophilic clays. The modified clay is then able to adsorb some organic compounds.

These mechanisms of contaminant immobilisation have been shown to be almost irreversible under common environmental conditions. It is hoped that this research will improve the

knowledge base on contaminant soil interactions in some Australian clays and may promote the use of reactive barriers in contaminated site remediation and attenuating layers in solid waste management.

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