Chemical Immobilisation of Chromium Wastes using Modified Smectite Clays (E-clays)

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1 Introduction

The treatment of contaminated soils and groundwaters containing significant concentrations of hexavalent and trivalent chromium presents a major challenge for remediation specialists. Chromite ore processing residues (COPR), which are waste materials arising from the chemical processing of ore to produce usable forms of chromium, have been historically used as infill material at a number of sites in Glasgow and elsewhere. The treatment of COPR requires a pragmatic approach, which aims to address not only the chemical properties of the waste material, but also the practical and logistical considerations, which are considerable. The application of modified clay (E-clay) technology offers a viable solution, with particular emphasis on the capability of the technology to treat groundwater / leachate arising from the source COPR material.

1.1 Background

Chromium can be found in the environment in a number of forms and oxidation states; hexavalent and trivalent forms of chromium are the most commonly isolated. Hexavalent chromium has been shown to be toxic to human health (Katz et al., 1994) and is relatively mobile, whereas trivalent chromium is comparatively less toxic and less mobile. Trivalent chromium exists as a cationic species (Cr^{3+}) and can be readily removed from solution by precipitation in alkaline media. Hexavalent chromium, however, exists in the anionic form and is soluble in both acidic and alkali media, predominantly forming (hydroxy) oxyanions including hydrogenchromate, $HCrO_4^-$; dichromate, $Cr_2O_7^{2-}$ and chromate, CrO_4^{2-}. The form of anion which predominates will depend primarily on the pH of the media and the respective chromium concentration (USEPA, 1992). As all forms are highly soluble, hexavalent chromium cannot normally be removed from solution without pre-treatment, which typically comprises reduction of hexavalent chromium to the trivalent form. Infiltration of rainfall and associated surface run-off on contaminated land sites often results in considerable leaching of hexavalent chromium into the underlying groundwater, which can then be spread to adjoining sites through a contamination plume. This is one of the major

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concerns identified on sites contaminated with chromium wastes.

COPR wastes contain a mixture of hexavalent and trivalent chromium. Hexavalent concentrations are significant, typically in the range 1,000 – 5,000 mg/kg (predominantly in the chromate form). Total chromium concentrations vary considerably but are typically in the range 2,500 – 25,000 mg/kg. COPR wastes also typically contain calcium oxide (used in the processing of the ore) imparting high alkalinity. The associated alkalinity is not conducive to the application of conventional (traditional) chromium reduction processes, which normally require acidic conditions for effective treatment. The residue material is a mixture of fused material and finer particulate waste matter. The fused material is finely porous with exposed chromite particles on the outer and inner surfaces. The material has the propensity to leach from all exposed surfaces. This presents a significant problem in developing an effective treatment methodology, as it is impracticable to achieve effective access of the treatment agent to the internal chromium sites within the core matrix. Consequently, there is an identified risk with the performance of remedial techniques that focus on the source contamination in isolation.

1.2 Traditional Treatment Technologies

Traditionally, hexavalent chromium has been treated in waste and effluent streams by chemical and electrochemical treatment processes, normally involving the reduction of hexavalent chromium to a trivalent form (typically in acidic media). A further treatment step is usually necessary to adjust the pH to the optimum for precipitation of trivalent chromium as the hydroxide (ideally pH 9).

There are a range of reducing agents that have been applied successfully for the treatment of chromium contaminated wastes/groundwaters. Reductants include ferrous compounds, reduced sulphur compounds, zerovalent iron, hydrogen peroxide and hydrazine. Sodium hydrosulphite (dithionite) can be used directly in alkaline conditions, but is not usually cost effective.

1.3 E-clays

E-clays are modified smectite clays, developed and commercialised by Envirotreat. Originally developed for the treatment of organic pollutants, E-clays have been adapted for the treatment of inorganic species and radionuclides. A specific form of E-clay is particularly suitable for the treatment of chromium wastes and polluted groundwaters. In most contaminated land scenarios, both cationic and anionic forms of chromium are usually present. For COPR wastes, the prime chromium pollutants are in the form of trivalent chromium (Cr^{3+}) and chromate (CrO_4^{2-}). The E-clay formulation must have the capability to

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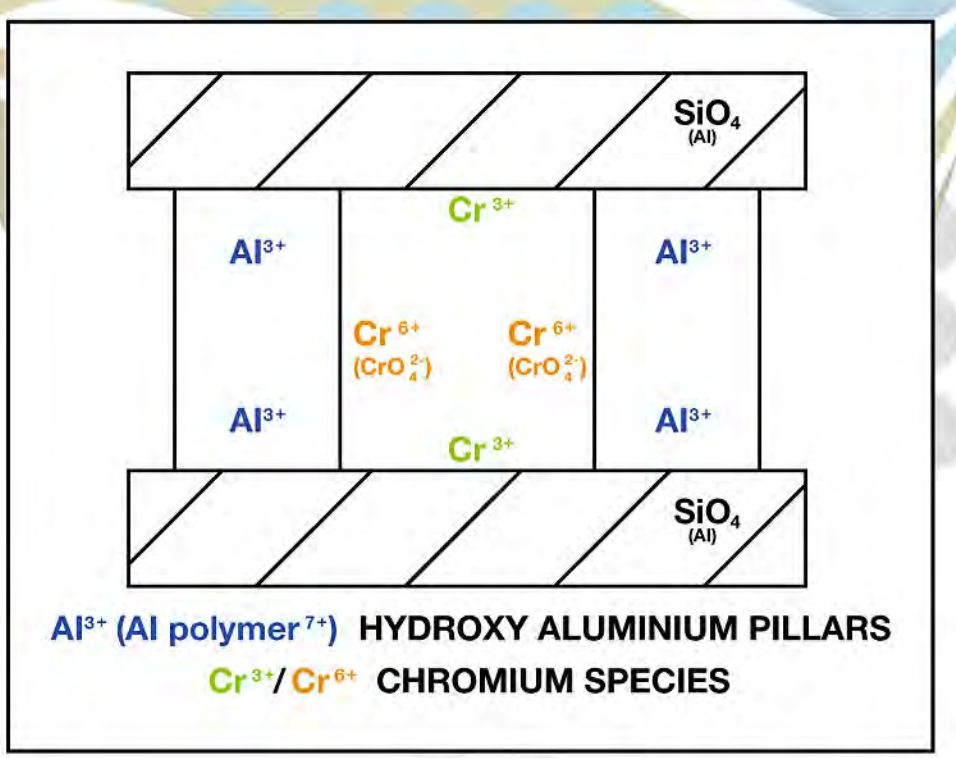
simultaneously absorb and chemically react with both forms (essential to provide a cost effective and practical solution involving a one-step remediation approach).

Partial modification of normal bentonite clay produces a 'pillared' inorganoclay with the capability of treating both cationic and anionic species. This form of inorganoclay is produced by the controlled stoichiometric intercalation of hydroxyaluminium cations. The hydroxyaluminium species have been shown to react with anionic forms of chromium (McLeod. Int. Comm. 1997). Cationic species, i.e. trivalent chromium, preferentially cation exchange at the residual reactive sites on the clay, displacing Ca^{2+} and/or Na^{+} cations. Pillared clays can be used in permeable reactive barriers (active containment systems).

Figure 1 is a diagrammatic illustration of a modified pillared inorganoclay (E-clay) showing mode of interaction with Cr^{6+} (CrO_4^{2-})/ Cr^{3+} species.

Figure 1. Modified pillared inorganoclay – mode of interaction with Cr^{6+} and Cr^{3+}.



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2 Treatment Trials

A number of laboratory treatability trials have been carried out to determine the efficacy of the E-clay technology for the treatment of chromium contaminated material. Trials were carried out using COPR waste sampled from the Glencairn Football Club, located in Rutherglen, Glasgow. These trials were carried out at the laboratories of Soletanche Bachy (SB), based in Paris. These trials formed part of a stabilisation evaluation project, supervised by Dames & Moore, UK.

2.1 Adsorption Treatability Studies

As the COPR waste was predominantly alkaline (pH 9.7 – 10.8), it was decided to use sodium chromate solution as an adsorbate. The prime focus at this stage was to evaluate the sorptive capabilities of selected potential absorbents including E-clays for the treatment of hexavalent chromium alone. The E-clay formulation utilised was a partially modified pillared inorganoclay. The mode of interaction with the chromate ion is assumed to be with the intercalated hydroxyaluminium cation. Unmodified smectite clays (bentonites) were also included in the study.

Comparative sorption trials were carried on a range of sorptive media and the results (as reported by SB) are as shown in Table 1. The Freundlich model was utilised to determine K and 1/n values. Straight -line isotherms were obtained for the E-clay formulation.

Table 1. Comparative Adsorption Capabilities of Potential Treatment Media

Media	K (L/g)	1/n	Media	K (L/g)	1/n
Bentonite 1		0.00	Bentonite 3	4.02E – 02	0.89
Bentonite 2		0.00	Bentonite 4	4.58E – 02	0.92
E-clay	1.76E + 00	0.40	Activated Carbon	5.25E – 02	0.85
Flyash	2.04E – 02	0.98	Sand	2.38E – 02	1.04
Slag	3.70E – 11	3.14			

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The results demonstrate that the E-clay formulation is an effective sorbent medium for hexavalent chromium. Unmodified bentonites exhibit minimal sorptive capabilities for hexavalent chromium. This can be further demonstrated by a comparison of sorptive data, as shown in Table 2. The volume of adsorbate utilised was 100 ml and the mass of sorbent was fixed for the purposes of this trial at 2.5g. The values for X/m represent the actual amount of chromate ion sorbed divided by the amount of sorbate utilised. The values for Q represent the sorptive capability in terms of milliequivalents per 100 grammes of sorbent (expressed as Cr^{6+}).

Table 2. Chromate Sorption – Comparative Data for E-clay and Unmodified Bentonite

Chromate Envirotreat Clay (E-clay)								
Initial Conc.		pH		Conc. at Equil. mg/l	X/m (mg/g)		Q' (meq/100g)	
Theoretic mg/l	Measured mg/l	Initial	At equil.		Theoretic	Measured	Theoretic	Measured
500	480.0	7.4	6.8	227	10.92	10.12	126	117
100	101.0	7.3	6.7	2	3.92	3.96	45	46
10	10	8.0	6.8	0.02	0.40	0.40	5	5
Chromate Unmodified Bentonite								
500	480.0	7.4	8.9	480	0.80	0.00	9	0
100	101.0	7.3	8.9	101	-0.04	0.00	0	0
10	10	8.0	9.0	10	0.00	0.00	0	0

2.2 Groundwater and Leachate

Further treatability studies were carried out by Envirotreat on COPR contaminated soils (Davies, T.J., 1999), focussing on both trivalent and hexavalent chromium. These studies included the treatment of groundwater and leachate, using modified inorganoclay (E-clay) formulations as per the generic structure as shown in Figure 1. Stoichiometric addition rates of E-clays were utilised for the treatment of cationic species. The results are as shown in Table 3.

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Table 3. Results of treatability studies on groundwater / leachate

	Ground Water Sample		Soil Stock Leachate Sample		
Contaminant Analysed	Untreated Sample – A (mg/l)	Treated Sample – B (mg/l)	Untreated Sample – C (mg/l)	Treated Sample – D (mg/l)	Untreated Sample – E (mg/l)
Cr^{3+}	144.1	4.5	8.5	0.20	0.57
Cr^{6+} ($Cr^{6+}O_4^{2-}$)	17.9	5.8	54.5	0.60	0.37
Total Cr	162	10.3	63	0.80	0.94
% Removal Rate (Cr^{3+})		97		98+	93+
% Removal Rate (Cr^{6+})		67		99+	99+

Sample A was a contaminated groundwater sample from the Rutherglen site (COPR waste). Both trivalent and hexavalent chromium were present within the groundwater sample. Trivalent chromium was the prime pollutant in terms of concentration. Hexavalent chromium was present (presumably in the chromate form) at relatively low concentration. As the sample was taken directly from the site, it is assumed that other ionic species were present in the groundwater, with the potential to compete for the active sites on the E-clay.

Sample B was a sample of groundwater treated with E-clay. The removal rate for trivalent chromium was 97%, from 144.1 mg/l to 4.5 mg/l. These results demonstrated the capability of the E-clay formulation to adsorb the cationic trivalent chromium species. The removal rate for hexavalent chromium was 67%, from 17.9 mg/l to 5.8 mg/l. Although satisfactory, the removal rate was lower than expected which could be due to the presence of competing anionic species in the groundwater sample.

Sample C was a sample of 'stock' leachate solution produced by leaching a sample of COPR waste in water in a 1:1 ratio. This was designed to represent a situation where the COPR material is in direct contact with a water plume. In this case, the majority of the leached chromium was in the hexavalent form.

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Treated leachate samples, D and E illustrate the effective removal of both hexavalent and trivalent chromium in solution. Both were treated with the designated E-clay formulation. The results showed a removal rate for trivalent chromium of 93 – 98% and a removal rate for hexavalent chromium of 99% respectively. The results for hexavalent chromium were consistent with the sorption trials carried out at SB.

2.3 Contaminated Soil Samples

Trials were also carried out on contaminated soil samples. Visual analysis of the contaminated soil showed that the majority of chromium (hexavalent and trivalent) waste was deposited in the form of hardened and fused aggregate material, intermixed within finer particulate waste matter. Extensive stabilisation trials were carried out using various chemical reduction agents and modified clays. It was concluded that it was not practically feasible to effectively treat pollutants within the core of the fused material (irrespective of the treatment technology and/or methodology employed), due to poor accessibility of the treatment reagent within the core matrix of the COPR material. Treatment of the external surfaces was feasible, with varying degrees of success. In essence, the treated fused material retains the potential to leach toxic hexavalent chromium. As with any treatment reagent / additive, the E-clay technology will only be effective on contact with the chromium pollutants.

2.4 Potential Applications of Modified E-clays

Modified E-clays can be applied as a specialist additive to a stabilisation / solidification treatment process, either *in-situ* or *ex-situ*. Pillared forms of the clays can be utilised as the treatment media in permeable reactive barriers / active containment systems (McLeod, N.A., 1998). For the treatment of COPR wastes, they can be applied as a 'one-step' treatment operation, having the capacity to treat both forms of chromium simultaneously, without the need for pre-treatment (in particular, pH adjustment).

The use of reactive barriers (either as a stand-alone remediation process or in conjunction with site capping) to treat contaminated groundwater / leachate is a cost effective and practical solution. Stabilisation of the source material may still be necessary if subsequent development of the site is planned (due to the poor physical properties of the material in this respect).

3. Conclusions

The treatment of chromium bearing waste materials is a difficult and complex problem. COPR wastes are

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particularly problematical due to the high alkalinity of the material, which is not conducive to the application of traditional treatment techniques.

The pragmatic application of modified smectite clays (E-clays) on a site-specific basis provides a viable solution. Treatability studies have demonstrated the potential applicability of E-clays, with particular emphasis on the treatment of groundwater / leachate.

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