Treatment of Groundwaters Contaminated with Radionuclides and Associated Pollutants – A Case Study

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1 Introduction

The following report is a summary of laboratory work carried out on contaminated groundwater samples taken from the Maqar Aquifer in Jordan. Envirotreat were requested to evaluate the efficacy of its proprietary E-clay®, technology utilising Jordanian clay minerals as the base material. Specialist E-clays® were developed with the prime objective of removing both anionic and cationic pollutants within the groundwater. The E-clay® technology was demonstrated to be effective in the treatment of all identified pollutants and can be viewed as a cost-effective and practical solution for the remediation of the Maqar well and other similarly polluted water resources in Jordan.

1.1 Background

Natural water is a valuable resource, particularly in semi-arid regions where there is often a high demand for scarce supplies. Because of this high demand, not only must water resources be protected, but there is also increasing pressure to utilise water which may not previously have been considered potable due to contamination; from either natural or artificial origins.

The modified clays (E-clays®) developed by Envirotreat Limited have been evaluated during laboratory-scale feasibility studies for the treatment of groundwater obtained from the Maqar well, Jordan. This water has been shown to contain various naturally-occurring radionuclides *viz.* uranium, radon and radium and enhanced concentrations of other associated toxic trace elements (predominantly selenium and molybdenum). One of the main aims of the study was to remove targeted contaminants from the Maqar well groundwater in order to meet the World Health Organisation (WHO) guideline drinking water standards shown below;

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Radon	<100 Bq l^{-1}
Radium	<0.2 Bq l^{-1}
Uranium*	<20 µg l^{-1}
Molybdenum	<50 µg l^{-1}
Selenium	<10 µg l^{-1}

*An arbitrary target devised for the purposes of these trials in the absence of a WHO guideline value

It is important to note that this type of contamination problem is not specific to this locality since uranium, radon and radium are part of the radioactive decay series of ^{238}U which is present naturally in many igneous and sedimentary environments.

Typical analyses of water sampled from the Maqar well are as shown in Table 1 below. It should be noted that the Maqar well has a quoted yield of 103 m^3 hr^{-1} and that concentrations of molybdenum and selenium shown in Table 1 were considerably lower than in the sample subsequently provided which was used in the laboratory treatment trials described hereafter.

Table 1: Analysis of target contaminants in Maqar well water

Element (Isotope)	Sample 1	Sample 2
Ra (228)	5.7 Bq l^{-1}	6.7 Bq l^{-1}
Rn (222)	833.0 Bq l^{-1}	1067.0 Bq l^{-1}
U	1186.63 ppb	1256.51 ppb
Mo	528.54 ppb	544.57 ppb
Se	10.19 ppb	87.82 ppb

Note: Concentration levels for molybdenum and selenium in the original analysis were considerably lower than those in the sample subsequently provided for laboratory treatment trials (see later Tables)

The primary contaminants of concern were shown to be predominantly present as anionic species;

Uranium:	$UO_2(HPO_4)_2^{2-}$	$UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_3^{4-}$
Molybdenum:	$HMoO_4^-$		
Selenium:	$HSeO_3^-$	SeO_3^{2-}	SeO_4^{2-}

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Radium was present in the conventional cationic form whereas radon was present in the gaseous form, in solution. The latter was not considered problematic since conventional degassing techniques could be employed to eliminate the gas from the water. Therefore, the treatment trials were focussed upon the ionic species present, although the removal of radium was not regarded to be an issue of concern in this instance since relatively low levels had been recorded. However, the applicability of conventional cation exchange systems were not viewed as particularly applicable given the competition from the range of cations naturally present in groundwater *e.g.* Na^{+}, Ca^{2+}, Mg^{2+} *etc.*

The E-clay® technology is applicable for treatment of groundwater since the clays may be pillared with hydroxyaluminium species. These pillars create adequate interlamellar spacing to accommodate the passage of contaminated water through the clay matrix, bringing contaminants in contact with relevant reactive species intercalated within the clay. These reactive species can be selected to provide an inorganophilic environment to chemically fix the contaminants within the substrate. The inorganophilic clay provides a medium for the effective treatment of both cationic and anionic species, by interaction with the intercalated species and/or cation exchange processes. Conventional smectite clays *e.g.* bentonite exhibit cation exchange properties which can be utilised in the treatment of some cationic species but the specificity can be further enhanced *via* the addition of interlayer reactive species. The clays may be either fully or partially modified, depending upon the nature and concentration of contaminants present. Full modification produces an inorganoclay with the capability of treating primarily anionic species, whereas partial modification produces an inorganoclay capable of treating higher proportions of cationic species in addition to anions. A range of clays may be suitable for use as the matrix which provides an added advantage to the technology since this flexibility may allow the use of natural resources of clays which may be present within the locality of contamination in some circumstances; should the properties of the clays be appropriate. Indeed a locally available Jordanian bentonite satisfied the desired chemical and physical criteria necessary to be used as a raw material and was thus used in the laboratory trials described below. The cation exchange capacity of the unmodified clay was shown to be *ca.* 56.6 meq 100 g^{-1} clay.

1.2 Treatment Rationale

The objective was to develop a comprehensive strategy which was both technically sound and logistically acceptable in order to address the identified contamination problems within the water resource. There was also a clear need to develop a cost-effective treatment solution.

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Assuming that the radon issue was addressed by conventional de-gassing techniques and was therefore not regarded to be within our direct remit, the strategy was focussed on ionic species present in the water supply. To treat the ionic contaminants effectively, it was thought that the technology must be capable of removing both cationic and anionic species on a selective basis. Given that the targeted pollutants were present at parts per billion concentrations and that the conventional water salts were typically present in much higher concentrations, the issue of selective removal was paramount to the design strategy.

The approach promulgated by Envirotreat was the use of modified pillared clays designed to remove both cationic and anionic species on a selective basis. The treatment technology is proprietary and is protected by appropriate Intellectual Property Rights (IPR). The initial view taken by Envirotreat was that uranium species would be preferentially removed due to the greater electronegativity of the anionic forms and *inter alia* the chemistry of uranium. Given this view, it was felt that a sequential treatment approach may have been necessary to effectively remove the molybdenum and selenium, which were present in addition to uranium.

The removal of ^{228}Ra by conventional cation exchange processes was not considered to be unduly problematical although the very low concentration of radium within the groundwater sample necessitated a more specialised approach in order to overcome perceived problems of competition with other cationic species particularly multivalent forms.

The initial strategy was to develop a single stage process targeted at the anionic species (in particular uranium). The approach adopted in terms of the overall rationale would then depend on the initial observations and results *etc.*

2 Treatment Trials

2.1 Adsorption Treatability Studies

a) Single clay treatment strategy (single-bed treatment trials)

These trials were carried out at Birmingham University in the presence of a representative of the British Geological Survey (BGS). A strict protocol was observed in accordance with that specified by BGS. Samples were taken by BGS and independently analysed at their laboratories. Two initial wet clay concentrations were used *viz.* 20 g l^{-1} and 2 g l^{-1}; equating to 7 g l^{-1} and 0.7 g l^{-1} dry clay weight respectively.

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In each case the wet clay material was suspended in a sample of the well water using conventional mixing techniques. Contact time was recorded in order to determine as far as practicably possible reaction times and kinetics *etc.* The samples were prepared for subsequent analysis by BGS in accordance with the stated protocol. The results obtained are tabulated and graphically represented in Table 2/Figure 1 respectively.

Table 2: Summary of single-bed treatment trials for U, Mo & Se

Dry Clay Addition Rate ($g\ l^{-1}$)	Contact Time (mins)	Analyte Concentration			Percentage Removal		
		U (μl^{-1})	Mo (μl^{-1})	Se (μl^{-1})	U	Mo	Se
0 (untreated)	-	1239	966	359	-	-	-
0.7 (anionic clay)	35	113	899	279	91	7	22
7.0 (anionic clay)	22	0.34	90	64	>99	91	82

The initial results clearly demonstrate effective removal of uranium using a single clay treatment strategy. It would appear that the ideal clay usage rate is in the order 1-3 g l^{-1} given that the 0.7 g l^{-1} clay addition was shown to be 91% effective. The results for molybdenum and selenium were largely as expected *i.e.* significant removal occurred with higher clay concentrations (albeit to a lesser extent than uranium) with minimal removal at lower clay concentrations. This observation appeared to support the view that a sequential treatment approach will be required. The initial trials appeared to indicate that uranium was selectively absorbed although there was no evidence from the data obtained from the initial trial to demonstrate that uranium was selectively absorbed over conventional water salts such as bicarbonate (which were present in much higher concentrations).

b) Sequential treatment strategy (sequential-bed treatment trials)

This approach was promulgated as a means to improve the removal efficiencies for molybdenum and selenium and ultimately to separate the cationic treatment process from the anionic. This was felt necessary in order to mitigate as far as possible any possible detrimental effects arising from combining two types of clays in one system (it was felt that a mixed bed approach would be unlikely to prejudice the cationic process as this is a conventional cation exchange technique; however, removal of anionic species involves chemical bonding processes which *may* be affected).

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A three-stage sequential treatment approach was therefore proposed as follows:

i) Removal of anionic species - particularly those of uranium;
ii) Removal of anionic species - particularly those of molybdenum and selenium;
iii) Removal of cationic species.

Whilst the sequential approach would involve a larger processing plant in theory it should be noted that the requirement for waste disposal should be largely unaffected in terms of overall volume *etc.* In the sequential approach the dedicated clays in each bed will by definition have longer usage times as they are focused on specific pollutants as opposed to combined loadings as would be experienced in a mixed bed strategy. The laboratory trials were carried out using similar techniques to those used for the single-bed approach. The results obtained are as shown in Table 3/Figure 2 (chart illustrates change in concentration following treatment with anionic clays).

Table 3: Summary of sequential bed approach treatment trials for U, Mo & Se

Dry Clay Addition Rate ($g\ l^{-1}$)	Contact Time (mins)	Analyte Concentration			Percentage Removal		
		U ($\mu g\ l^{-1}$)	Mo ($\mu g\ l^{-1}$)	Se ($\mu g\ l^{-1}$)	U	Mo	Se
0 (untreated)	-	1239	966	359	-	-	-
i) 2.6 (anionic clay bed 1)	7.5	*	*	*	*	*	*
ii) 2.1 (anionic clay bed 2)	7.5	<0.05	41	14	>99	>97	>99
iii) 1.6 (cationic clay)	15	<0.05	26	<10	>99	>98	>99

* No analysis at this stage – samples analysed following treatment in second anionic clay bed (15 mins cumulative contact time)

The results obtained clearly demonstrate that the sequential approach for anion removal achieves effective removal of all the targeted anionic species. The increased removal of the molybdenum and selenium species with relation to the results obtained following single-bed treatment are clear if the data in Tables 2 & 3 are compared.

c) Mixed bed strategy (mixed-bed treatment trials)

Following the initial trials, it was decided to evaluate the efficacy of a mixed bed strategy focussing primarily on radionuclides *i.e.* uranium and radium. The "mixed bed" approach comprises anionic and cationic clays within the same bed.

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It was decided to investigate a range of dry clay addition rates with a view to finding optimum levels for the treatment of anionic species, as the objective was to focus on uranium almost exclusively. Accordingly, three sets of addition rates were investigated: these were equivalent to dry addition rates of a) anionic clay 0.75 g l^{-1} / cationic clay 1.0 g l^{-1}, b) anionic clay 1.5 g l^{-1} / cationic clay 2.0 g l^{-1} and c) anionic clay 3.0 g l^{-1} / cationic clay 4.0 g l^{-1}. Contact time was accurately controlled to within a target of less than 15 minutes. As with the single-bed trials, the laboratory trials were carried out at the University of Birmingham in the presence of a representative of BGS. A full analysis was carried out on each treated sample and on the untreated groundwater sample. The results are tabulated and graphically represented in Tables 4, 5 & 6 and Figures 3, 4 & 5.

Table 4: Summary of mixed bed approach treatment trials for U, Mo & Se

Dry Clay Addition Rate (g l^{-1})	Contact Time (mins)	Analyte Concentration			Percentage Removal		
		U ($\mu g\ l^{-1}$)	Mo ($\mu g\ l^{-1}$)	Se ($\mu g\ l^{-1}$)	U	Mo	Se
0 (untreated)	-	>1250	866	354	-	-	-
0.75 (anionic) + 1.0 (cationic)	13	40.9	818	272	>97	6	24
1.5 (anionic) + 2.0 (cationic)	14	87.6	830	290	>93	4	18
3.0 (anionic) + 4.0 (cationic)	14	8.63	804	233	>99	7	34

Table 5: Summary of mixed bed approach treatment trials for a range of anions

Dry Clay Addition Rate (g l^{-1})	Contact Time (mins)	Analyte Concentration					
		HCO_3 (mg l^{-1})	F (mg l^{-1})	Cl (mg l^{-1})	Br (mg l^{-1})	NO_3 (mg l^{-1})	SO_4 (mg l^{-1})
0 (untreated)	-	255	0.18	81	0.23	4.49	65.7
0.75 (anionic) + 1.0 (cationic)	13	256	0.16	93.8	0.26	4.56	65.4
1.5 (anionic) + 2.0 (cationic)	14	255	0.17	101	0.24	5.44	66.5
3.0 (anionic) + 4.0 (cationic)	14	246	0.13	122	0.23	5.18	68.8

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Table 6: Summary of mixed bed approach treatment trials for a range of cations

Dry Clay Addition Rate ($g\ l^{-1}$)	Contact Time (mins)	Analyte Concentration							
		Ba ($mg\ l^{-1}$)	Ca ($mg\ l^{-1}$)	Si ($mg\ l^{-1}$)	Mg ($mg\ l^{-1}$)	K ($mg\ l^{-1}$)	Na ($mg\ l^{-1}$)	Sr ($mg\ l^{-1}$)	Ra ($Bq\ l^{-1}$)
0 (untreated)	-	0.103	46.6	6.92	46.1	2.4	35.8	0.418	10.5
0.75 (anionic) + 1.0 (cationic)	13	<0.002	0.37	4.58	37.2	0.76	115	0.001	<0.13
1.5 (anionic) + 2.0 (cationic)	14	<0.002	0.26	3.67	28.8	0.77	139	0.001	<0.13
3.0 (anionic) + 4.0 (cationic)	14	<0.002	0.18	1.71	18.4	0.99	167	0.001	<0.13

The results clearly demonstrate effective removal of both radionuclide species (uranium and radium). WHO target guidelines were achieved for both species utilising a dry clay addition rate of 3.0 g l^{-1} (anionic clay) for uranium and 1.0 g l^{-1} (cationic clay) for radium. As expected, relatively low removal rates for molybdenum and selenium were observed. Although not present at a significant concentration in the untreated sample, the level of strontium was reduced considerably even with the lowest clay addition rate. This is of relevance given the possibility of the treatment of strontium contaminated waters. It should be noted that, for uranium, molybdenum and selenium, there would appear to be an anomaly in all of the results obtained utilising 1.5 g l^{-1} of anionic clay as illustrated. It is considered that there may be some experimental or analytical error as the results for all of the three anionic species are higher than those for the 0.75 g l^{-1} addition rate by a similar proportion, *i.e.* the uptake was seemingly greater for the lower clay addition rate. Notwithstanding this issue, the results obtained for the 3.0 g l^{-1} addition rate achieved the arbitrary WHO target guideline for uranium with a reasonable safety margin. With regard to radium, effective removal down to less than detection levels was achieved for all the treated samples.

The results obtained for conventional cationic species; in particular, calcium, magnesium and sodium clearly demonstrate the principle of cationic exchange as effected in both the residual sodium for the anionic clay and the cationic clay. In simple terms, sodium is released into the treated ground water samples and replaced by calcium, magnesium and to a lesser extent potassium.

The selective absorption and removal of uranium in particular, is clearly demonstrated when comparing the uranium removal rate to that of the prime anionic salts within the water *i.e.* bicarbonate, chloride and sulphate. At an addition rate of 3.0 g l^{-1} (anionic clay) the percentage removal rate of bicarbonate is only 3.5 %, whereas the concentrations of both chloride and sulphate actually increase in solution (the latter phenomenon is to be expected as chloride anions in particular will be present on the clay surface as this salt is used in the clay modification process). Given that the conventional anionic salts are present in the original ground water sample at a typical concentration of 400 mg l^{-1} overall, which is significantly higher

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than uranium by a factor of over three hundred (typically 1.2 mg l^{-1}), it is fairly evident that uranium anions are preferentially and selectively absorbed, even in situations where other competing anions predominate. This observation will ensure that a cost-effective strategy can be adopted which focuses primarily on targeted species. It should be noted that the same argument also applies to molybdenum and selenium (albeit to a lesser extent) where percentage removal rates are still significantly higher than those observed for bicarbonate *etc.*

The clay treatment strategy was also effective in removing other cationic divalent/multivalent species, in particular barium, strontium, iron, manganese and silicon. The rate of uptake for silicon was significantly less than that observed for calcium *etc.* which is not to be expected bearing in mind that silicon is multivalent *i.e.* Si^{4+} and theoretically more strongly attracted to the clay than Ca^{2+} *etc.*

It should be noted that the ultimate daughter product from radon decay *i.e.* ^{210}Pb will be a cationic species and potentially toxic. Given the short half-life of ^{222}Rn, it is reasonable to assume that the ground water will be contaminated with ^{210}Pb. The results achieved for other cationic species indicate that lead should be effectively removed.

The analysis of both total cationic and anionic species demonstrates the effect of adding additional anionic species into the treated water samples as a result of contacting same with the modified clay particles. The results indicate that, in this case, the presence of residual chloride ions within the modified clay matrix has increased the overall chloride loading within the ground water (in *pro rata* quantities depending on the clay addition rate). If this is perceived to be a problem for a particular site, it may be necessary to "purify" the modified clay prior to use with treated water or alternatively the modified clay could be produced using a non-chloride based salt, although the chloride method is preferred. However, in this respect it should be noted that the drinking water standard in the UK for chloride is 400 mg l^{-1} which is considerably higher than that observed in the trials for a 3.0 g l^{-1} (anionic clay) clay addition rate *i.e.* 122 mg l^{-1}. From the results obtained in the treatment trials using a "non-purified" clay the chloride loading in the treated water samples was found to increase at an approximate rate of 14 mg l^{-1} for each gl^{-1} addition of modified clay. On this basis, clay purification prior to use may not be necessary but would be addressed on a site-specific basis.

In order to maintain electro-neutrality the total cation levels within the treated water samples have increased by approximately *pro rata* amounts. The overall stoichiometric calculation clearly shows that the increased anion levels have been compensated by increased amounts of sodium ions going into solution (in excess of the expected stoichiometric balance). Refer to Table 7 for data.

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Table 7: Data relating to ion-exchange in solution

Dry Clay Addition Rate ($g\ l^{-1}$)	Contact Time (mins)	Analyte Concentration			Percentage Removal		
		U (μl^{-1})	Mo (μl^{-1})	Se (μl^{-1})	U	Mo	Se
0 (untreated)	-	1239	966	359	-	-	-
0.7 (anionic clay)	35	113	899	279	91	7	22
7.0 (anionic clay)	22	0.34	90	64	>99	91	82

3 Proposed Applications and Conclusions

One major advantage of the clay technology is that the specific contaminants are removed from the water into the clay matrix which simplifies the subsequent waste disposal operation. However, due to the concentration of the radionuclides within the clay following the treatment process, elevated levels of radioactivity in the treatment agent would require specific handling measures to be adopted. It is suggested that the contaminated water could undergo an initial degassing stage in order to remove the radon gas (if present) followed by the percolation of the water through the treatment beds containing the clays deemed appropriate for the contaminants present. The treatment beds would be formulated on a site-specific basis; with the range of contaminants and concentrations dictating the type and quantity of treatment agents used. In order to aid safe handling and disposal of the spent treatment beds, they could be in modular form, encased in a material capable of minimising the permeation of ionising radiation into the surrounding environment *e.g.* concrete. A parallel arrangement of beds would allow rapid exchange from a spent to a fresh set of treatment materials. The spent clay material could be solidified using cementitious materials within the outer concrete cell if necessary and disposed of in a suitable repository. Conventional, less specific, separation processes such as reverse osmosis could also utilised as a separate final polishing stage in the system to remove excess levels of the cations and anions not removed by the clays.

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Figure 1
Analyte Concentrations vs. E-Clay Addition Rates for U, Se & Mo
(Single Bed Approach - Anionic Clay Only)

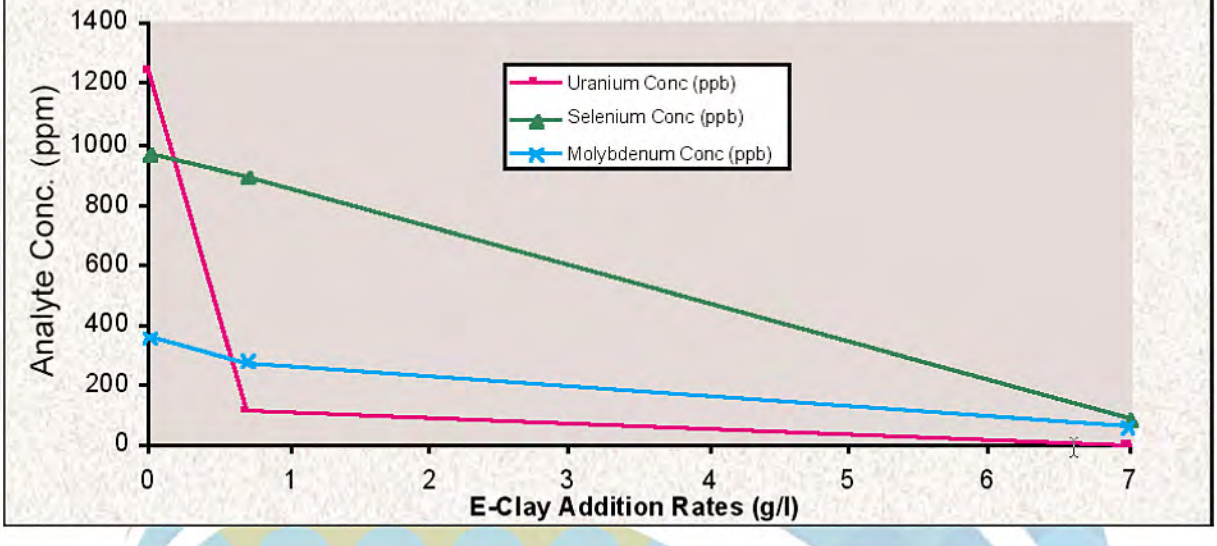

Figure 2
Analyte Concentrations vs. E-Clay Addition for U, Se & Mo
(Sequential Treatment Approach - Cationic and Anionic Clays)

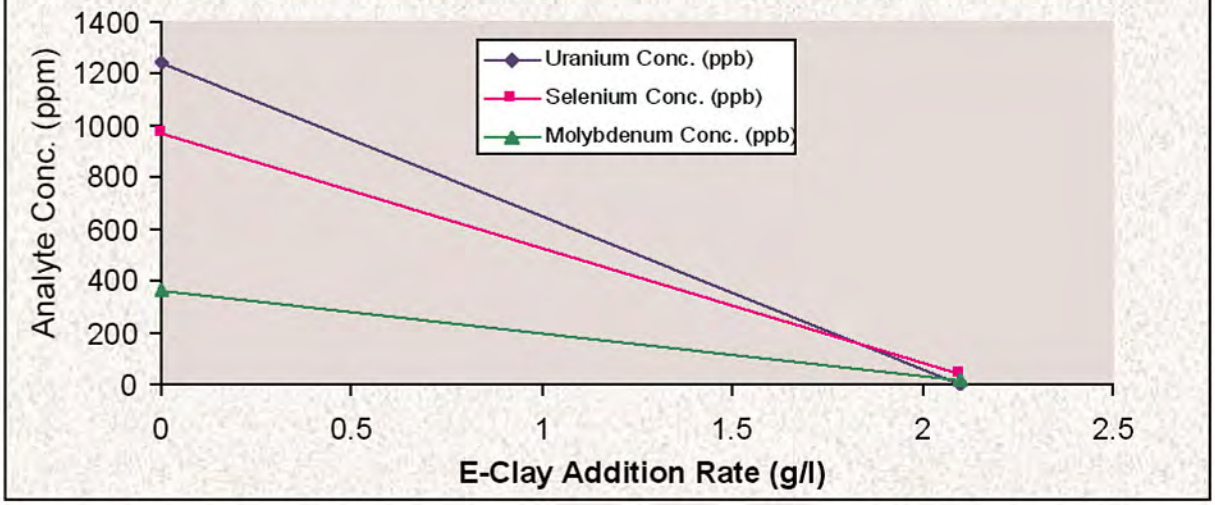

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Figure 3
Analyte Concentrations vs. E-Clay Addition Rates for U, Se & Mo (Mixed Treatment Approach - Cationic and Anionic Clays)

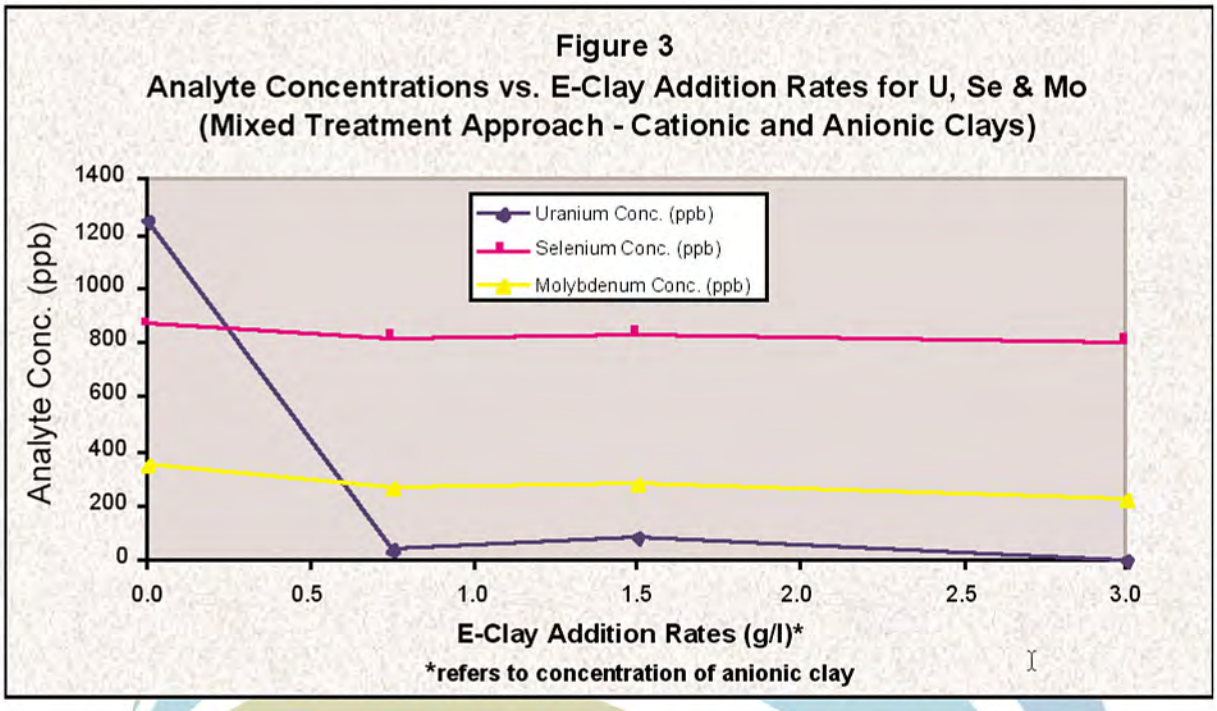

Figure 4
Analyte Concentrations vs. E-Clay Addition Rates for a Range of Anions

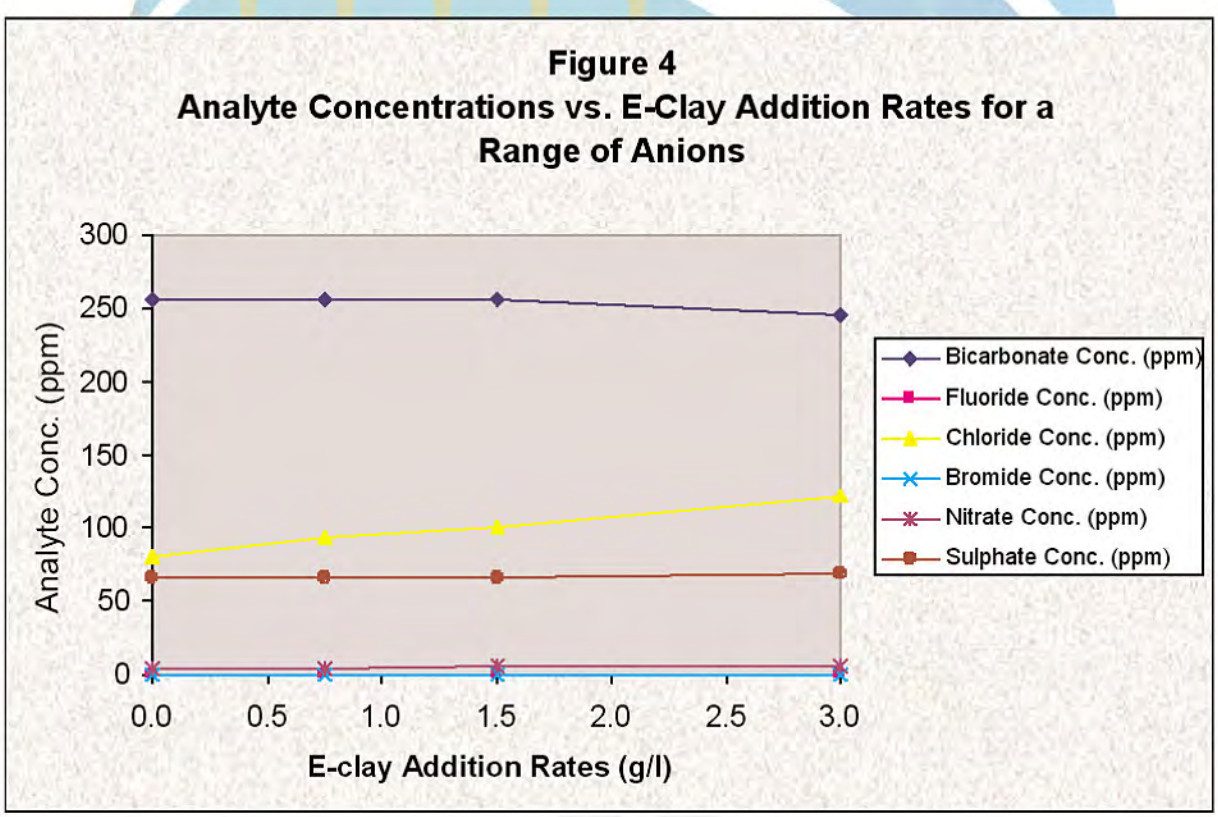

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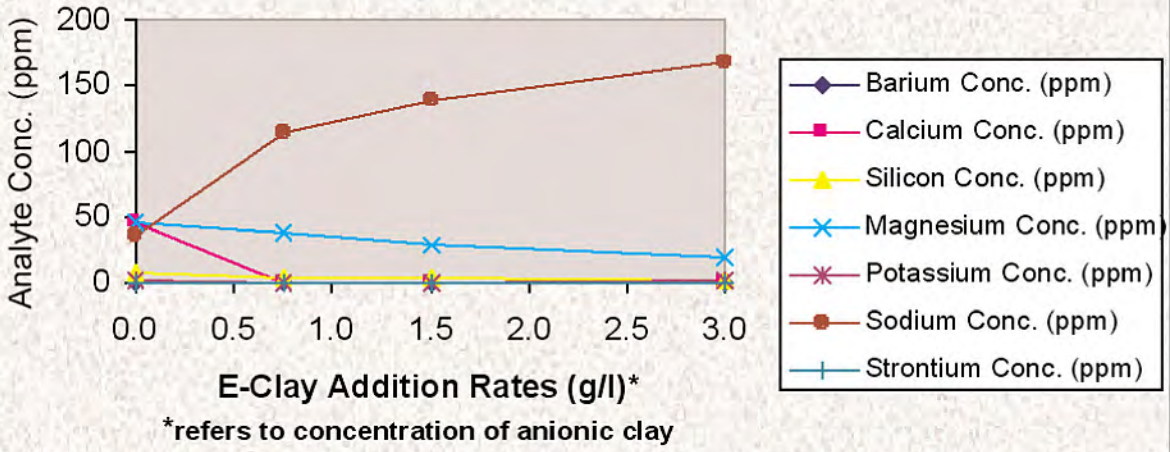
Figure 5
Analyte Concentrations vs. E-Clay Addition Rates for a Range of Cations



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