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## Assesment of Hexavalent Chromium stabilization in artificially contaminated soil using Geosta as a secondary binder

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The aim of this study was to investigate the effect of a secondary binder (Geosta) as a stabilizer on the geotechnical properties of Cr+6 contaminated soils with the use of S/S technology and to evaluate the efficacy of different mix designs via the Static Diffusion Test. Artificial contamination with Cr+6 was applied in four representative samples of soil material, weighting approximately 15 Kg each. The initial chromium concentration per cube was estimated at 128.5 mg/l and all mix designs studied were shown to be capable of reducing hexavalent chromium concentrations from 96 to 99%. The mix design which contained 400 g of Geosta, proved to be the most effective since the lowest release of chromium with maximum chromium retention (99.4%) was documented. Mix designs with 200 and 300 g of Geosta were considered to be successful in Cr+6 immobilization (with a total of 99.1 and 99% retention ability, respectively), however it was proved that the quantity of secondary binder used in a mix design is not proportional to its chromium retention capability.

### 1 INTRODUCTION

Millions of tons of chromium wastes are discharged from tanning, electroplating, wood treatment, metallurgy and plating industries each year (EPA United States, 2000). Sites adjacent to these industries could be highly contaminated with Hexavalent Chromium and the only reason for that is the improper handling of wastes from these industries. Excess deposits of hexavalent chromium in the fields can impose major risks to human and livestock occupying the surrounding area (Alloway, 1995; Bell, S. & McGillivray 2007). These areas could be identified as areas with a high potential for groundwater contamination since they impose a great risk to potable supplies of the surrounding ecosystem. Hence, there is an emerging need to develop a treatment method to minimize the risk of chromium contaminated land. As such, environmentally motivated remediation efforts have become increasingly relevant to solve this problem.

Treatment techniques such as Solidification and Stabilization (S/S) are becoming increasingly important in the contaminated land sector while they increase awareness of the environmental impact arising from its activities and resulting materials. The principal behind the S/S technology is based on its ability to reduce or even eliminate the mobility of hazardous contaminants -within a hazardous waste stream- while its effectiveness is measured via the application of leaching tests in the final material. Environmentally acceptable S/S materials can also be used for construction purposes such as bricks for pavements, secondary road sub-base systems, car park facilities and

many others. What seems to be of high importance prior to the implementation of S/S technology is the treatability study, during which the appropriate binder system is selected. The binder system is site and contaminant specific and is dependent upon the properties of the end products, the nature of the material in use and the specific target values for the desired contaminant (Dermatas and Meng, 2003).

In the current investigation, Geosta was chosen as a secondary stabilization agent and which exists in a powder form. It contains zeolites, alkalis and a mixture of other complex elements in minor concentrations and its chemical composition is shown on Table 1.

Table 1. Chemical composition of Geosta

Chemical Compound	Proportion (%)
NH <sub>4</sub> Cl	5
NaCl	20
FeCl <sub>3</sub>	2
C	1
MgCl <sub>2</sub>	22
KCl	25
CaCl <sub>2</sub>	15
Others	10
Total	100

An aqueous solution of Geosta liberates exchangeable ions including K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> which through isomorphous substitution replace the R-OH and R-COOH ion groups in organic soils (Omotosho, 2005). When Geosta is used with Portland cement it enhances complete hydration and strength development (Paria *et al*, 2006).

The main aims of this study were to investigate the effect of Geosta as a stabilizer on Cr (VI) artificial contaminated soil with the use of S/S technology and also to evaluate the efficacy of various secondary binder quantities via the Static Diffusion Test (in accordance with the norm EA NEN 7375:2004 protocol).

## 2 MATERIALS AND METHODS

The experimental program for solidified and stabilized soils consisted of the combination of one primary binder (Portland cement) at stable quantity (5% by dry weight of the soil) and one inorganic secondary binder (Geosta) at 1.3, 2 and 2.6 % (by dry weight of soil).

For the purpose of this study, a known concentration of Chromium Hexavalent (Cr (VI)) (522 mg/kg or 900 mg/l) was prepared in order to artificially contaminate 15 Kg of concrete sand (sandy soil). Solidification of the S/S specimens was achieved by adding Portland cement (type I 35/A) while stabilization of the samples was attempted with the use of a commercially available product (Geosta). Various proportions of Geosta were tested in a total of three admixtures while their stabilization effectiveness (treatment performance) was determined via the Static diffusion test (tank test) and compared versus a cement-based S/S mixture. Table 2 summarizes the mix design of the total 4 admixtures with Geosta being the only variable component.

Table 2. Mix design of each batch

Mixtures	Contained Materials	Proportions
Mix No1 (Control)	Soil	15 Kg
	Portland Cement	750 g (5%)
	Chromium solution	522 mg/kg or 900 mg/l
	Water	1.2 litres
Mix No2	Soil	15 Kg
	Portland Cement	750 g (5%)
	Chromium solution	522 mg/kg or 900 mg/l
	Water	1.2 litres
Mix No3	Geosta	200 g
	Soil	15 Kg
	Portland Cement	750 g (5%)
	Chromium solution	522 mg/kg or 900 mg/l
Mix No4	Water	1.2 litres
	Geosta	300 g
	Soil	15 Kg
	Portland Cement	750 g (5%)
	Chromium solution	522 mg/kg or 900 mg/l
	Water	1.2 litres
	Geosta	400 g

Standard proctor compaction tests were carried out on each composite soil-cement-geosta mixture. Following the production of the S/S material, the compacted soil samples remained in the mould for an additional 24 hours (solidification stage) and then were placed in transparent polyethylene bags in order to reduce/avoid moisture loss.

In total 28 moulds of S/S treated material, were produced (7 moulds for each mix design). Including the duplicates, a total of eight (8) solidified cubes were selected to proceed to the next laboratory stage for the assessment of Cr (VI) leaching behavior. The solidified samples, were immersed in eight (8) different clear plastic containers, with W (mm): 240, H (mm): 180 and L(mm): 290 dimensions, which were filled with distilled water at a Liquid to Solid (L/S) ratio equal to 5. More specific, the volume of each specimen (100x100x100mm) was one (1) litre while the volume of the added distilled water was 5 litres. According to the protocol, the water in each tank needed to be replaced eight times and at specified intervals. The times at which the water had to be replenished were 0.25, 1.0, 2.25, 4.0, 9.0, and 16.0 days. Before, the scheduled replenishments of water, leachant samples were obtained and the pH of the leachant was measured. The samples collected for chemical analysis, were preserved after collection in Envirobottles and at a temperature between 18 and 22°C.

In total 48 samples were collected for further chemical analysis. 12 samples corresponded to each of the four (4) different mix designs, which in their turn represented 6 samples for each selected S/S specimen. The presence of Cr(VI) in each sample was measured by Ultra Violet-visible (UV-Vis) Spectrophotometry. The spectrophotometric approach that was chosen relied on the specific reaction of Cr (VI) with 1.5-diphenylcarbazide (1.5-DPC). The colorimetric method is based on the oxidation of 1.5-DPC to diphenylcarbazone by Cr (VI), leading thus to the formation of a red-violet complex, while its absorbance is measured through UV/Vis spectrophotometry. When the reaction is performed in alkaline solution, Cr (VI) partially reacts with 1.5-DPC and a red color solution is produced. However, as the pH solution becomes lower, Cr (VI) is more

inclined to oxidize another substance (Bone *et al*, 2004) and for this reason fully oxidation of 1.5-DPC is achieved only in acidic solutions where the red-violet color is produced. For this reason samples were acidified with H<sub>2</sub>SO<sub>4</sub> (pH~1) prior further analysis. This method measures only the presence of diphenylcarbazone complex (and therefore, Cr<sup>+6</sup> concentrations) and conversion of trivalent to hexavalent chromium was not required.

### 3 RESULTS AND DISCUSSION

As part of the test procedure, pH, Cr (VI) concentration, Geosta variability and time cycles are compared and further discussed. The results of leaching tests are accompanied by table and figure presentations in order to interpret information in a quick and easy manner. For identification purposes, samples that were tested for their leaching behavior were labeled as shown on Table 3, and they will be referred as such throughout this section.

Table 3. Sample labeling

Mixtures	Sample Identification*
Mix No1	B <sub>1</sub> S <sub>1</sub>
(No GEOSTA present)	B <sub>1</sub> S <sub>2</sub>
Mix No2	B <sub>2</sub> S <sub>1</sub>
(200g of Geosta)	B <sub>2</sub> S <sub>2</sub>
Mix No3	B <sub>3</sub> S <sub>1</sub>
(300g of Geosta)	B <sub>3</sub> S <sub>2</sub>
Mix No4	B <sub>4</sub> S <sub>1</sub>
(400g of Geosta)	B <sub>4</sub> S <sub>2</sub>

#### 3.1 pH variation

The pH values in the static diffusion test in Table 4 show that there is not a considerable difference between the samples. The average pH values of the leachant throughout the tank test ranges between 10.7 and 11.7, presenting thus, much greater values than the initial pH of the distilled water (pH~7). Mix design parameters seem to not have any effect upon pH variation among the samples and the small differences in pH values could be attributed to the pore structure of the material surface.

Table 4. Average pH values between 0.25 and 16 days.

Sample	Average pH
B <sub>1</sub> S <sub>1</sub>	10.8
B <sub>1</sub> S <sub>2</sub>	11.7
B <sub>2</sub> S <sub>1</sub>	11.4
B <sub>2</sub> S <sub>2</sub>	10.7
B <sub>3</sub> S <sub>1</sub>	11.2
B <sub>3</sub> S <sub>2</sub>	11.3
B <sub>4</sub> S <sub>1</sub>	11.2
B <sub>4</sub> S <sub>2</sub>	11.2

### 3.2 Hexavalent Chromium

The leaching characteristics of hexavalent chromium in the static diffusion test are very similar, between samples of the same group, in terms of the metal release versus time (Table 5).

Table 5. Chromium Hexavalent concentrations (mg/l).

GROUP	Sample	Days					
		0.25	1	2.25	4	9	16
B <sub>1</sub>	B <sub>1</sub> S <sub>1</sub>	0.179	0.473	0.754	0.599	0.701	1.266
	B <sub>1</sub> S <sub>2</sub>	0.762	0.274	0.725	0.701	1.447	0.968
B <sub>2</sub>	B <sub>2</sub> S <sub>1</sub>	0.156	0.237	0.241	0.147	0.269	0.174
	B <sub>2</sub> S <sub>2</sub>	0.145	0.217	0.427	0.158	0.371	0.145
B <sub>3</sub>	B <sub>3</sub> S <sub>1</sub>	0.154	0.473	0.096	0.099	0.226	0.176
	B <sub>3</sub> S <sub>2</sub>	0.244	0.154	0.127	0.088	0.172	0.194
B <sub>4</sub>	B <sub>4</sub> S <sub>1</sub>	0.296	0.122	0.066	0.079	0.072	0.118
	B <sub>4</sub> S <sub>2</sub>	0.439	0.127	0.09	0.057	0.109	0.099

It is evident that the samples of group B<sub>4</sub> showed a greater effectiveness in chromium immobilization than the other three groups since they contained higher concentrations of hexavalent chromium within their matrix. B<sub>4</sub> samples demonstrated a uniform chromium release throughout the whole leaching procedure this could be taken as an evidence of almost identical preparation and curing conditions (Figure 1).

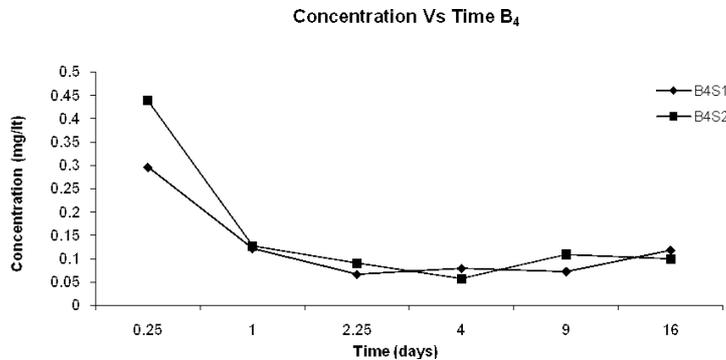


Figure 1. Relation between the amount of leached hexavalent chromium (mg/l) and test duration (days), in Group B<sub>4</sub>

The fact that group B<sub>4</sub> showed an intense leaching status at the beginning of the test, followed by drastic chromium retention around the values of 0.1 mg/l can also be used as proof for the above statement. The initial increased presence of hexavalent chromium in the water could be attributed to either carbonation of the specimens or premature zeolite crystallization. The latter however, seems to be more probable since the quantity of Geosta contained within these specimens was greater than that of the B<sub>2</sub> and B<sub>3</sub> groups, for this reason it needed more time to reach full hydration. Portland cement requires 28 days (Bone *et al.*, 2004) of curing in order to reach full hydration while Geosta 90 days. While curing time seemed to have affected the B<sub>4</sub> group specimens, it was also evident that even a partial hydration (after 1.25 days of contact with the hydrating agent) of the Geosta powder was capable of immobilizing and “locking” the hexavalent chromium within its

zeolite matrix. The overall performance of B<sub>4</sub> specimens in chromium retention can be seen in figure 2, which shows the accumulative leaching for all eight samples.

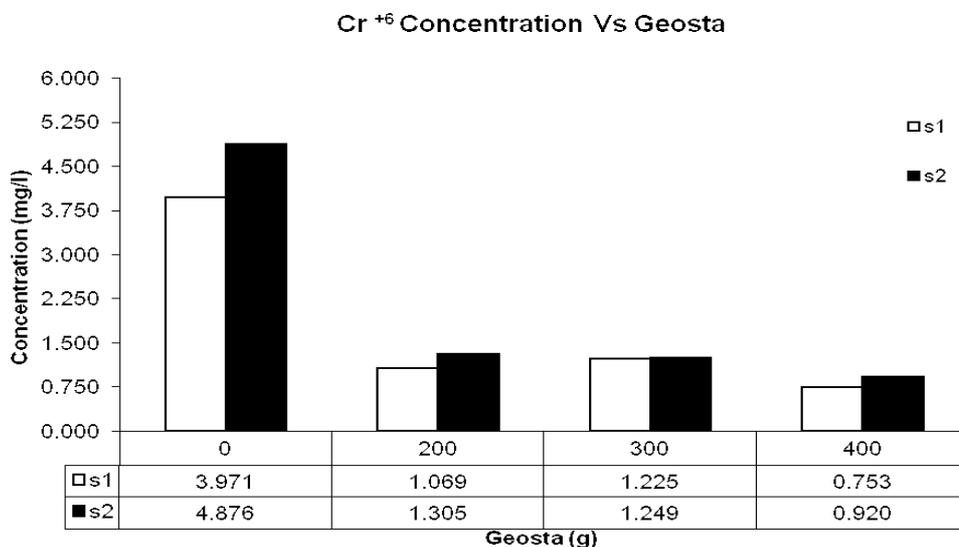


Figure 2. Total Hexavalent chromium concentration versus Geosta quantity

Since Group B<sub>4</sub> maintained the overall chromium leaching level below 1 mg/l it can be argued that it achieved optimum performance in chromium retention. However, all four (4) mixture designs managed to retain chromium contamination within the overall study quantitative target of 25mg/kg Cr+6 (ICRL, 1987) while the most effective mixture was proved to be the one with 400g of Geosta.

Taking into consideration the almost identical leaching behavior of the B<sub>3</sub>S<sub>1</sub> and B<sub>3</sub>S<sub>2</sub> samples we can assume that faults during the material preparation were kept to a minimum. Furthermore study of Figure 3 which demonstrates the average daily leaching rate (ADLR) per each sample can support the above statement. The ADLR was calculated by dividing the accumulative chromium concentrations of each sample, with the total duration (in days) of the leaching test. What was observed was that B<sub>3</sub> samples exhibited an identical ADLR while B<sub>2</sub> and B<sub>4</sub> samples showed a small variation (between 0.05 and 0.07 mg/l/day). B<sub>1</sub> group samples on the other hand, show a much greater deviation of 0.028 mg/l/day. Therefore, it could be argued that sample preparation and material density could play an influential role in the leaching behavior of S/S products. It is important to mention that ADLR values represent the chromium leakage rate only within the specified period of the test, since they do not reflect field conditions. The leaching rate of S/S field materials depends on more complicated mechanisms such as weathering and temperature therefore any data regarding ADLR values should be taken cautiously into consideration (Van Der Sloot, 1997).

As it has been stated previously, the leaching characteristics of groups B<sub>2</sub> and B<sub>3</sub> can be considered an unexpected finding. Figure 3 demonstrates that the overall leaching performance of sample B<sub>2</sub>S<sub>1</sub> proved to be more effective in chromium retention than samples B<sub>3</sub>S<sub>1</sub> and B<sub>3</sub>S<sub>2</sub>. A possible explanation behind this result could lie within the sample preparation procedure, the carbonation effect, the correct performance of the leaching test or even the treatment period of the samples. For this reason, interpretation of the results for B<sub>2</sub> and B<sub>3</sub> groups should be made with caution since it requires further experimentation for the acquisition of a solid conclusion.

In general, it cannot be assured that the overall effectiveness in chromium retention by the four (4) different mixture designs will be maintained when applying different test conditions. Different

test conditions may have implications on the surface area of S/S samples, leachant characteristics, L/S ratio and/or pre-treatment of samples (Bone *et al*, 2004). Therefore, it needs to be stated that the results presented in this thesis are only valid for the specific conditions on which the methods (S/S and leaching test) were performed.

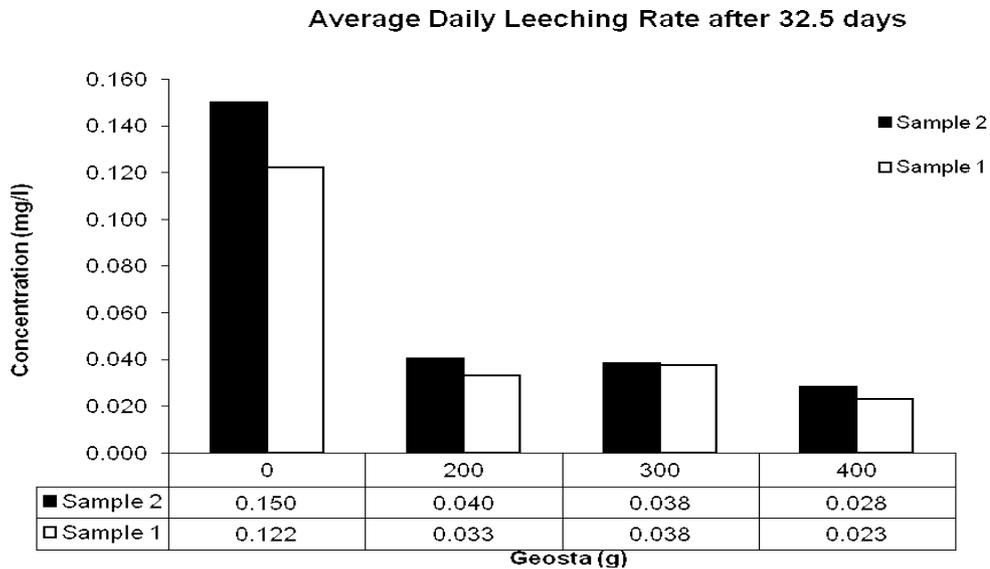


Figure 3. Average daily leaching rate per each sample versus Geosta quantity.

#### 4 CONCLUSION

S/S treatment is a very effective method in reducing potential hexavalent chromium leakage and it would be applicable primarily to sites where the principal risks concern humans and surrounding ecosystems. S/S treatment could be defined as a low-tech technology and it seems to be applicable where relatively fine to granular materials are to be treated.

All mix designs studied in this project have shown to be capable of reducing hexavalent chromium concentrations by up to 99%. B<sub>1</sub> mix design is the least effective when compared to the other three designs since it shows the largest release of chromium in both of its samples. On the other hand, B<sub>4</sub> mixture is the most effective, presenting the lowest release of chromium amount and a maximum performance of 99.4% chromium retention.

Mix designs B<sub>2</sub> and B<sub>3</sub> were considered to be successful in hexavalent chromium immobilization with a total of 99.1 and 99.0 retention ability, respectively. It was initially expected that the quantity of secondary binder would be proportional to its chromium retention capability. However, the tank leaching method revealed that both B<sub>3</sub> samples demonstrated lower chromium “fixation” in comparison to B<sub>2</sub>S<sub>1</sub>. The weaker performance of B<sub>2</sub>S<sub>2</sub> could indicate faults during the preparation and/or leaching procedure and for this reason a cautious approach is essential during the analysis of the obtained results.

Although pH variations tend to be one of the most important parameters that control leaching behavior of S/S materials, in the present study pH variations were not observed. The presence of the binders (Portland cement and Geosta) in the mix designs were considered responsible for the presence of the high alkaline pH environment. It is believed that the alkaline environment favored or accelerated the crystallization of the zeolite matrix of Geosta.

Geosta binder systems can be considered as effective stabilizing agents in S/S treatment. In laboratory conditions, the combination of 750g of Portland cement and 400g of Geosta was proven to be the most effective mix design regarding chromium retention. This observation however was

noted in comparison with the other three (3) mixtures. The addition of 200g and 300g of Geosta was found to be less effective when compared to that of 400g.

Faults during the preparation, leaching assessment and chemical analysis of the samples, could affect their behavior and alter their physical and chemical properties. Regarding the sample preparation procedure, these faults could be related to inappropriate compaction, ineffective plastic bag sealing, unintentional plastic bag damage during material transportation, incorrect sample storage temperature and/or short curing period. In relation to the tank leaching test, errors might have occurred during water replenishments leading to prolonged contact of the sample with atmospheric CO<sub>2</sub> (carbonation effect). The case of leachant aeration by an unintentional container lid removal could also be considered, although it is unlikely. Finally, in relation to sample chemical analysis, the prolonged preservation of the samples could lead to pH alterations, which in their turn could result in changes in the relative concentrations of the oxidation states of chromium.

Hexavalent chromium was successfully incorporated within the C-S-H matrix of Portland cement and the addition of Geosta powder in the mixture designs, demonstrated a further incorporation of hexavalent chromium in the zeolite crystals of Geosta.

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