

## TDP bulletin

CL:AIRE Technology Demonstration Project (TDP) bulletins provide a summary of CL:AIRE approved Technology Demonstration Projects. TDPs have passed through the CL:AIRE application and review process, and represent demonstration for the specific conditions in which they are applied. This bulletin describes a field trial undertaken to assess three methods of application of calcium polysulphide to treat hexavalent chromium contamination in Glasgow.

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## *In Situ* 'Deliverability' Trials Using Calcium Polysulphide to Treat Chromium Contamination at Shawfield, Glasgow

### 1. INTRODUCTION

This bulletin reports on a field trial that was undertaken to assess the effectiveness of three *in situ* methods of application of calcium polysulphide (CaS<sub>x</sub>) for the treatment of hexavalent chromium (Cr(VI)) associated with Chromite Ore Processing Residue (COPR).

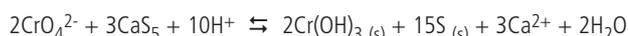
From the late 1800s until the 1960s, the J & J Whites chemical works in Shawfield, Glasgow was one of the world's largest producers of chromium. Over the period of operation, an estimated 1.5M m<sup>3</sup> of COPR, arising from the production process was used as landfill material in the south-eastern areas of the city (Farmer *et al.*, 2006). COPR is a geochemically complex material which is characterised by a high pH and elevated concentrations of both total Cr and Cr(VI). The majority of chromium consists of trivalent chromium (Cr(III)), the most common form within the natural environment, which is of low toxicity and an essential element in human nutrition. At neutral to moderately alkaline pH it is relatively immobile but becomes more soluble at very high or low pH levels. In contrast, Cr(VI) is a recognised human carcinogen, with mutagenic potential and has a corrosive effect on skin and mucous membranes. It is also highly mobile across a broad range of pH (CL:AIRE, 2007).

The areas impacted by COPR include the 63 ha Shawfield site, which is at the forefront of the Clyde Gateway initiative, one of the largest and most ambitious regeneration projects in Scotland, with a core development area covering 838 ha and a private investment programme in the order of £1.6 billion. The public sector partners are Glasgow City Council, South Lanarkshire Council, Scottish Enterprise, and the Scottish Government. Delivery of the regeneration is being undertaken by Clyde Gateway; for details go to their website <http://www.clydegateway.com>.

Whilst the risks to human exposure from COPR deposition can largely be mitigated by engineered solutions such as capping impacted areas, significant pollutant linkages remain with regards to contaminated groundwater and surface waters, most notably with respect to the River Clyde. These are largely driven by the occurrence of COPR below the water table, where it had been deposited as backfill in areas used for clay extraction. A remedial solution was therefore sought to address Cr(VI) associated with such residues.

Traditional treatment methods have typically employed a chemical reducing agent to convert Cr(VI) to Cr(III), examples being ferrous sulphate, sodium bisulphite, sulphur dioxide, zero valent iron, although physical and biological methods have also been employed. These have been reviewed in an earlier CL:AIRE publication (CL:AIRE, 2007). However it became apparent, through a

series of field trials conducted in the 1990s that most of these methods were unable to satisfactorily meet the challenge of COPR-associated Cr(VI) (Bewley *et al.*, 2000). Following an extensive research programme led by the University of Edinburgh and the Macaulay Institute (now James Hutton Institute), to characterise some of the geochemical properties of COPR and bench-scale testing (Farmer *et al.*, 2006), one particular reducing agent, CaS<sub>x</sub>, was identified as being particularly effective in the treatment of COPR-based Cr(VI), the reaction being as follows:



Following the success of bench-scale testing (Graham *et al.*, 2006), an *ex situ* 'skip-based' field trial was conducted using soils impacted by COPR (Bewley & Clarke, 2010). This demonstrated reductions in both soil and more importantly, leachable concentrations of Cr(VI), from approximately 800 mg/kg to less than 2 mg/kg and from 80 mg/l to 0.3 mg/l respectively, using an application rate of 0.035 L/kg of 29% CaS<sub>x</sub>. The effectiveness of polysulphides in COPR treatment was confirmed by independent researchers in New Jersey, where similar issues exist (Chrysochoou *et al.*, 2008).

A simple, gravity based field trial was later conducted at Shawfield, in which approximately 21 m<sup>3</sup> of 29% CaS<sub>x</sub> solution was injected through a single well over 3 days. Whilst the anticipated physicochemical changes were observed in the immediate vicinity of the well, the reactivity of CaS<sub>x</sub> resulted in blockage of the formation assumed to be a result of the formation of reaction products, calcium compounds, S, and Cr(OH)<sub>3</sub>.

Whilst CaS<sub>x</sub> was therefore identified as being an effective reagent, a key issue determining the success of application was therefore its deliverability. As such, a field trial was devised to evaluate the deliverability of CaS<sub>x</sub> in the *in situ* treatment of Cr(VI) associated with COPR.

### 2. OBJECTIVES AND SCOPE OF TRIALS

The overall objective of the trials was to assess the effectiveness of a number of methods of CaS<sub>x</sub> application (deliverability) in the treatment of COPR-related Cr(VI) contamination associated with both soil and groundwater, using groundwater re-circulation, direct injection and deep soil mixing.

These three methods of CaS<sub>x</sub> application were trialled on the Shenkins Yard site, bounded by Clydeside Road, Millcroft Road and Camp Road in the Shawfield area of Glasgow as shown on Figure 1.

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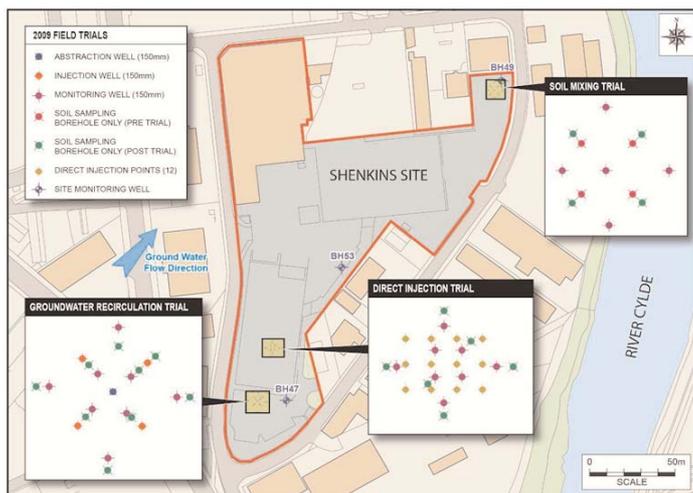


Figure 1: Site plan showing location of trial plots, and monitoring well network

The works were commissioned by Clyde Gateway Developments Ltd. URS Corporation Ltd (URS) was appointed as consultant to Clyde Gateway and undertook the detailed design and specifications for the trials. Implementation of the trials took place during August 2009.

The commercial formulation of CaSx was sourced as BSP CASCADE®, (29% CaSx) from Best Sulfur Products, Fresno, CA, USA and transported to the UK in 200 gallon tanks ('totes') to a local chemical manufacturer where it was batched into the appropriate concentrations for each trial and delivered to site in Intermediate Bulk Containers (IBCs). These were stored on site in a dedicated compound, protected by a bund, and delivered to each of the trial areas as required by the contractor responsible.

Details of the soil and groundwater treatments applied and the monitoring regimes are summarised in Table 1.

### 3. GROUNDWATER RE-CIRCULATION TRIAL

#### 3.1 Description of Approach

A schematic for this trial is presented in Figure 2.

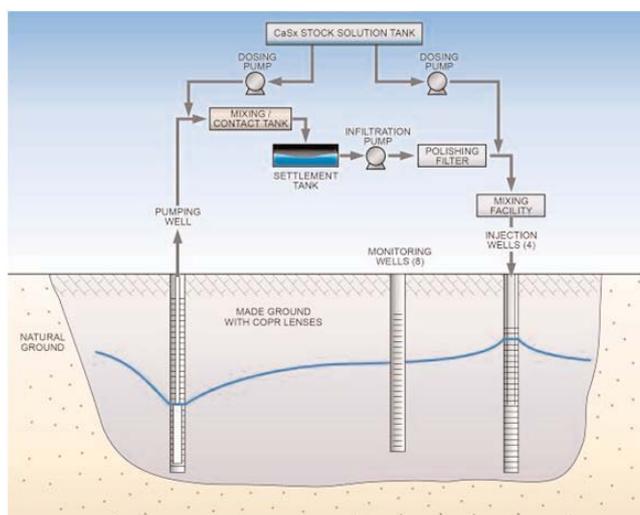


Figure 2: Schematic section of groundwater re-circulation trial

The system consisted of a single 150 mm diameter abstraction well located in the centre and four 150 mm diameter injection wells located at the corners of the test area, drilled using cased solid stem auger techniques (Figure 3 illustrates the abstraction well and some of the injection wells).

Table 1: Trial plot details, application rates and soil and groundwater monitoring plan

	Groundwater re-circulation	Direct injection	Soil Mixing
Dimensions of treatment area	5m x 5m	6m x 4m	5m x 5m
Approximate depth of treatment	1.5-6m	0.4-9.6m	0-10m
Theoretical saturated volume within plot	113m <sup>3</sup>	230m <sup>3</sup>	250m <sup>3</sup>
Volume of 29% CaSx applied	20m <sup>3</sup>	20m <sup>3</sup>	16m <sup>3</sup>
Total volume of diluted CaSx applied during trial	200m <sup>3</sup>	40m <sup>3</sup>	32m <sup>3</sup>
Duration of application	10 days	6 days	3 days <sup>a</sup>
No. of abstraction wells (AW)	1	N/A <sup>b</sup>	N/A
Depth of abstraction well	6m bgl	N/A	N/A
No. of injection wells (IW)	4	N/A	N/A
Depth of injection wells	6m bgl	N/A	N/A
No. of soil sampling boreholes pre-application	8	8	9
No. of boreholes completed as monitoring wells within plot (MW)	4	8	0
No. of boreholes completed as monitoring wells immediately outside trial area	4	0	4
No. of soil sampling boreholes post-application in trial area	7 <sup>c</sup>	6	5
No. of post application boreholes constructed as monitoring wells in trial area	0	0	1
Range of installation depths of monitoring wells	3.0-7.9m bgl	4.5-10m bgl	4.0-9.5m bgl
No. of soil samples/soil leachates pre-trial	12/8	12/8	12/8
No. of soil samples/soil leachates post trial	8/8	8/8	8/4
No. of groundwater samples pre-trial	13	8	4
No. of groundwater samples post-trial per round	8-13 <sup>d</sup>	8	4-5 <sup>e</sup>
No. of groundwater monitoring rounds during & post application	7	8	4
Days from application to final sampling	23 days	21 days	18 days

a Excludes trial columns; b Not applicable; c Excludes one borehole which met with refusal; d All wells (AW+IW+MW) during initial and final post application sampling; MW on intermediate samplings; e Includes central well within plot at final sampling

A submersible pump unit was installed for the abstraction of groundwater from the well located in the centre of the test area, the rate being controlled using a manual flow control valve. The abstracted groundwater was discharged to a mixing/contact tank where it was mixed with just sufficient CaSx to treat the assumed concentration of Cr(VI) present within it. This was approximately equivalent to a one hundred-fold dilution of the stock 29% CaSx, which based on the studies of Graham *et al.* (2006), would be sufficient to treat in excess of 50 mg/l Cr(VI). A maximum pre-trial concentration of 34 mg/l Cr(VI) indicated that this was likely to be more than adequate (Table 2). The treated groundwater

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Figure 3: Groundwater re-circulation trial with abstraction well in foreground

was transferred from the mixing tank to a downstream settlement tank, from where it was pumped through a polishing filter unit (designed to achieve 150 micron particle size filtration), with a manual control valve being used to adjust the pumping rate as required. The filtered stream was then dosed with the estimated concentration of CaSx required to achieve *in situ* treatment of Cr(VI) with a further facility ensuring adequate mixing prior to discharge. The CaSx-supplemented water stream was then discharged via suitable pipe work and a distribution manifold system to the infiltration wells.

Sample points were provided immediately following abstraction and prior to the second dosing of CaSx. Flowmeters providing an indication of cumulative flow volumes were located immediately following abstraction and prior to discharge and additionally on the lines from the two dosing pumps.

Circulation of groundwater commenced on August 4<sup>th</sup> 2009. Initially, groundwater only was re-circulated until the system was tested and balanced to meet the injection rates required. It was noted that the abstraction rate dropped from 2.4 m<sup>3</sup>/hr to 1.8 m<sup>3</sup>/hr in the first 24 hours of operation with a steady but notable decline thereafter to 1.13 m<sup>3</sup>/hr. The circulation of CaSx solution was completed by day 10 (August 13<sup>th</sup>) and the system was flushed with clean water for 24 hours. Following completion, a backwashing trial carried out on the abstraction well indicated an improvement in abstraction rate to near that at the start. This resulted in a slight increase in the head in the injection wells.

On completion of the trial, there was no evidence of precipitate in the settling tanks of the system as a whole. Whilst there was a decrease in the abstraction rate, it was not necessary to pressurise the system to meet the circulation rates required.

Analysis of samples for total Cr and Cr(VI) was undertaken according to in-house methods that were based on APHA/AWWA/WEF (1998) and US EPA Methods 3050B, 3060A and 7196 (US EPA, 2007). Due to the formation of a precipitate, dilution of aqueous samples was necessary in a number of instances, which resulted in a raised reporting limit for Cr (VI) (from 30 to 300 µg/l: see Table 2).

Both total Cr and Cr(VI) concentrations in soil were significantly reduced following treatment, the former potentially reflecting a mobilisation through the treatment regime, though the reduction averaged less than 20%. Cr(VI) was reduced by 86% on average in soil, though leachate concentrations were highly variable and no reduction was apparent (it was noted however that the three deepest soil samples below the water table all returned non-detectable leachate concentrations of Cr(VI) following treatment). Soil pH was relatively unchanged. Groundwater concentrations of both total Cr and Cr(VI) demonstrated a rapid reduction following treatment, and this was sustained over the 24 days of the trial (Figure 4).

The mean concentrations presented are somewhat conservative estimates, given the raised reporting limits due to the requirement for dilution, but both total Cr and Cr(VI) were significantly lower following treatment. There was no significant difference in concentrations between wells indicating that the radius of influence of the reagent extended to at least the monitoring wells outside the trial plot.

The behaviour of other key metals forming anionic species that had previously been identified as having a potential to increase in mobility under conditions of high pH is also illustrated in Figure 4. In the case of arsenic (As), selenium (Se), and to a lesser extent vanadium (V) there was an increase in concentration following injection. For As and V, that appeared to be transient and concentrations subsequently decreased to pre-treatment levels, though Se remained more elevated. Potentially increased mobilisation of Se through this specific approach may therefore be an issue for further review in the context of overall risks to controlled waters, though it may be mitigated by more moderate pH levels outside the source area.

Table 2: Concentrations of total Cr, Cr(VI) and pH before and after groundwater re-circulation trial implementation

Matrix and analyte <sup>g</sup>	Unit	Pre-trial				Post trial <sup>a</sup>				Maximum		Stats. <sup>b</sup>	Sig. <sup>c</sup>	
		Mean	±	SD <sup>d</sup>	n <sup>e</sup>	Mean	±	SD	n	Pre-trial	Post-trial			
Soil	Total Cr	mg/kg	6063	±	4802	12	4950	±	4472	8	15,000	14,000	t	Yes
Soil	Cr(VI)	mg/kg	148	±	246	12	20	±	24	8	750	67	WMW	Yes
Soil	pH		10.4	±	1.2	12	10.4	±	1.8	8	12	12	t	No
Leachate <sup>f</sup>	Total Cr	mg/kg	76	±	84	8	203	±	278	8	200	810	WMW	No
Leachate	Cr(VI)	mg/kg	82	±	92	8	188	±	265	8	220	770	WMW	No
Groundwater	Total Cr	µg/l	16,935	±	43,825	13	51.54	±	149.77	13	160,000	550	WMW	Yes
Groundwater	Cr(VI)	µg/l	7416	±	12,530	13	<300	±	0	13	34,000	<300	WMW	Yes
Groundwater	pH		8.9	±	0.9	13	10.4	±	0.3	13	12	11	WMW	No

a: day 24 data; b: Student's t test (t) or Wilcoxon Mann Whitney (WMW) rank test; c: significant reduction in concentration according to specified test; d: standard deviation; e: number of samples; f: as determined using a CEN 10: 1 leach test (BS EN 12457-2; 2002); g: Estimated analytical uncertainty: Cr(VI) in water 6.8%, total Cr in water 8.9%, Cr(VI) in soil 11.6%, total Cr in soil 6.5%

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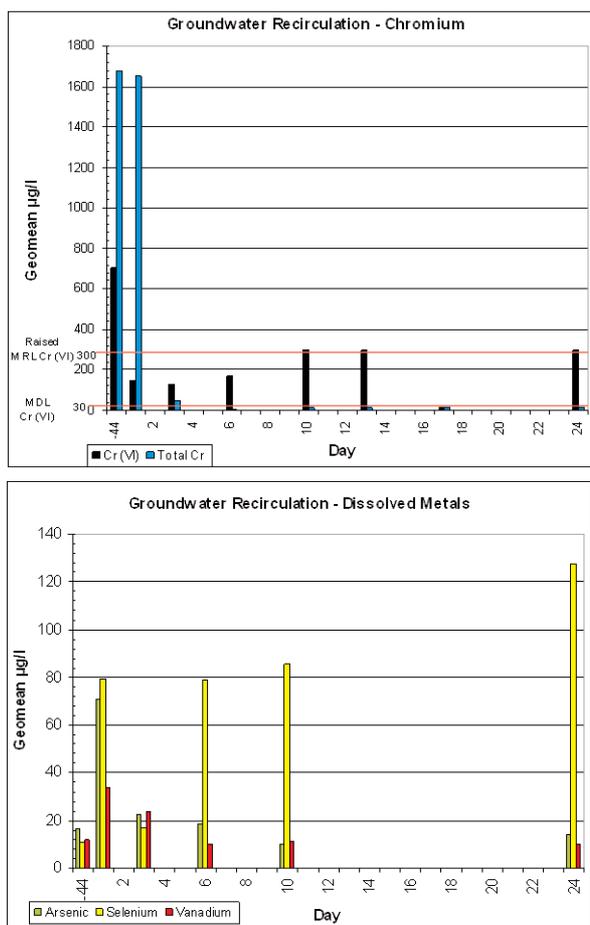


Figure 4: Concentrations of Total Cr, Cr(VI), As, Se and V prior to and following implementation of groundwater re-circulation trial

## 4. DIRECT INJECTION TRIAL

### 4.1 Description of Approach

A schematic for this trial is presented in Figure 5. The method involved a direct push approach whereby drive rods were advanced to approximately 9.5 m below ground level whereupon CaSx was injected at approximately 200 mm intervals as the rods were withdrawn. When 'daylighting'<sup>1</sup> of CaSx through the 50 mm monitoring wells and other injection holes occurred, injection was temporarily ceased and the CaSx level in the wells allowed to drop before recommencing injection. The injection element of the trial was completed on 9<sup>th</sup> August 2009. Injection of the CaSx commenced on August 3<sup>rd</sup> using a small track mounted injection rig, which was replaced by a larger and more efficient apparatus on August 5<sup>th</sup> (Figure 6).

### 4.2 Results

Data from the direct injection trial are presented in Table 3.

Both the total Cr and Cr(VI) decreased significantly in soil following injection, the latter by two orders of magnitude. Soil pH decreased by one unit from 11.9 to 10.8 following treatment.

Soil leachate data were again highly variable, but in the case of Cr(VI), a statistically significant reduction was observed, with half of the post treatment test samples returning concentrations below the reporting limit.

<sup>1</sup> 'Daylighting' is a term used in the direct injection of substances into ground, in which the substance takes a preferential pathway to the surface (instead of being laterally distributed from the point of injection), either directly up through the borehole in which it is being injected (i.e. along the side of the injection rod) or up through an adjacent borehole or well (i.e. it progresses laterally from the injection point then upwards once the injected substance meets the well or borehole).

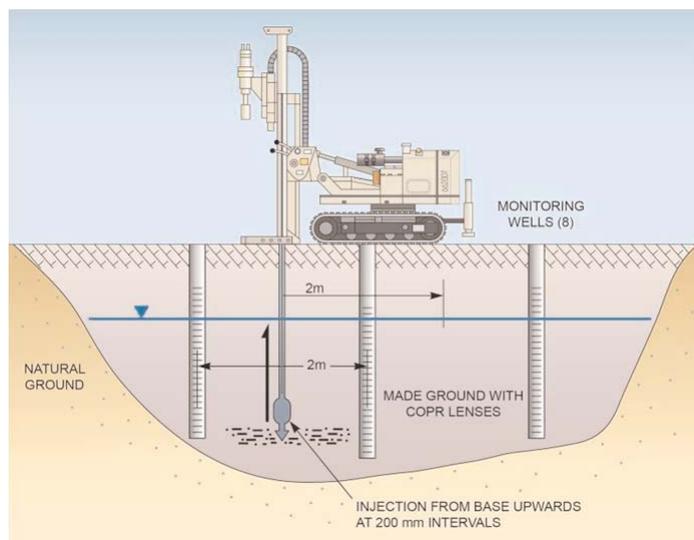


Figure 5: Schematic section of direct injection trial



Figure 6: Rig used for direct injection trial

The groundwater data for Cr(VI) were commonly subjected to a raised reporting limit (which explains the apparent discrepancy between these and the total Cr data, which have a lower limit), but were nonetheless significantly lower (non-detectable) following treatment (Figure 7).

There was a transient elevation in arsenic, vanadium and selenium (especially the latter), but these returned to pre-trial levels by day 20. In contrast to the soils data, the groundwater pH increased from 11.5 to 12.3 by the end of the trial.

## 5. SOIL MIXING TRIAL

### 5.1 Description of Approach

A schematic for this trial is presented in Figure 8.

The trial employed the use of a 54 tonne piling rig fitted with 900 mm auger drill bit with the facility for pumping CaSx solution through the tip during augering (Figure 9). The process involved the breaking up of the soil and application of the CaSx using the continuous flight auger to create a series of overlapping cylindrical columns of 10 m in length, at 900 mm centres, equating to 39 columns across the whole of the treatment zone. A total of 820 litres of diluted CaSx solution were delivered to each 10 m column, at a rate of approximately 228 litres per minute.

It had been anticipated that this process would result in bulking of the ground rather than settlement. However, when a trial soil mixing column was prepared

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Table 3: Concentrations of total Cr, Cr(VI) and pH before and after direct injection trial implementation

Matrix and analyte <sup>g</sup>		Unit	Pre-trial				Post trial <sup>a</sup>				Maximum		Stats. <sup>b</sup>	Sig. <sup>c</sup>
			Mean	±	SD <sup>d</sup>	n <sup>e</sup>	Mean	±	SD	n	Pre-trial	Post-trial		
Soil	Total Cr	mg/kg	13,525	±	9781	12	9712	±	7210	8	38,000	23,000	t	Yes
Soil	Cr(VI)	mg/kg	354	±	454	12	2.09	±	4.11	8	1100	12	WMW	Yes
Soil	pH		11.9	±	0.9	12	10.8	±	1.1	8	13	12	WMW	Yes
Leachate <sup>f</sup>	Total Cr	mg/kg	130	±	218	8	435	±	863	8	570	2500	WMW	No
Leachate	Cr(VI)	mg/kg	150	±	256	8	80	±	190	8	670	550	WMW	Yes
Groundwater	Total Cr	µg/l	0.02	±	37.72	8	10.88	±	1.64	8	110	14	WMW	No
Groundwater	Cr(VI)	µg/l	835	±	1249	8	<30	±	0	8	3800	<30	WMW	Yes
Groundwater	pH		11.5	±	0.2	8	12.3	±	0.2	8	12	12	t	No

a: day 20 data; b: Student's t test (t) or Wilcoxon Mann Whitney (WMW) rank test; c: significant reduction in concentration according to specified test; d: standard deviation; e: number of samples; f: as determined using a CEN 10: 1 leach test (BS EN 12457-2; 2002); g: Estimated analytical uncertainty: Cr(VI) in water 6.8%, total Cr in water 8.9%, Cr(VI) in soil 11.6%, total Cr in soil 6.5%

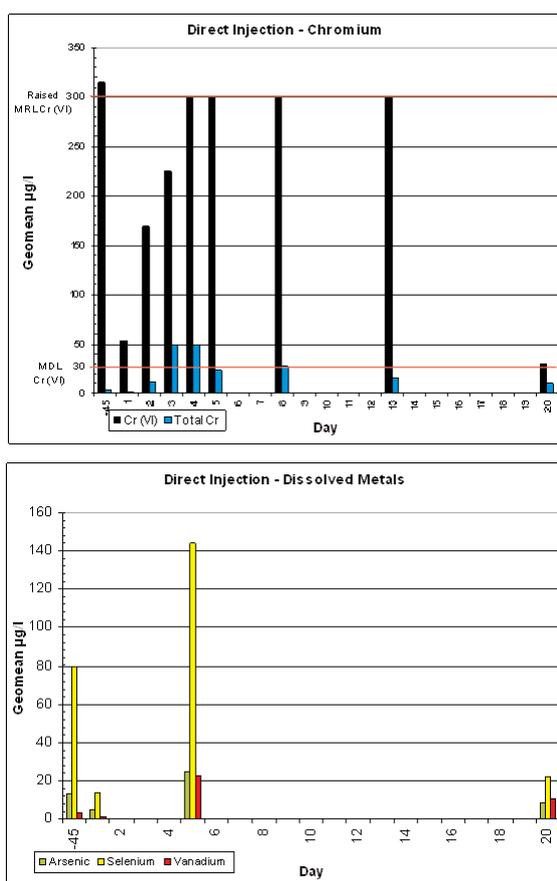


Figure 7: Concentrations of Total Cr, Cr(VI), As, Se and V prior to and following implementation of direct injection trial

using water outside the trial area, this resulted in a hole being formed in which the ground surface sank by approximately 1 m. It was therefore necessary to import approximately 80 tonnes of Type II fill across the 25 m<sup>2</sup> area of the trial in order that the ground could be filled on completion of the soil mixing columns following settlement (Figure 10).

## 5.2 Results

Data from the soil mixing trial are presented in Table 4.

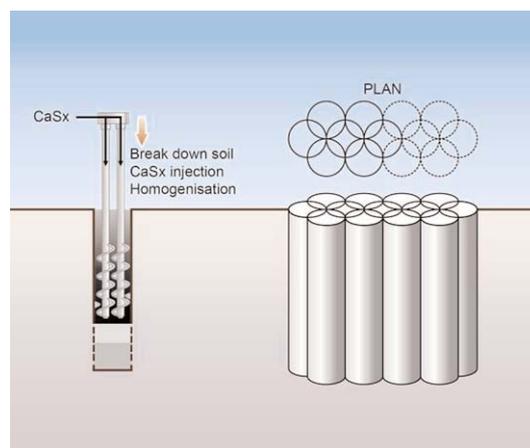


Figure 8: Schematic section of soil mixing trial

Whilst there was a significant decrease in total Cr by around 28% in soil, the greatest reduction took place with Cr(VI), with all post treatment samples returning non-detectable concentrations from starting levels of up to 1300 mg/kg. Soil pH increased slightly over the trial from 11.5 to 12. The effects on soil leachable concentrations were also relatively clear cut, for both the total Cr and Cr(VI) data with significant reductions in both cases, the majority of samples returning post treatment concentrations below, or very close to, the method reporting limit.

Because of the nature of the trial, the groundwater data are derived from wells located immediately outside the trial plot, apart from the inclusion of the central well post treatment, so the lesser degree of reduction in both total Cr and Cr(VI) needs to be interpreted in this light. Nonetheless, reductions of both total Cr and Cr(VI) were statistically significant (Table 4; Figure 11). There also appear to have been some transient mobilisation of chromium during the treatment (day 5 of the treatment), though this returned to pre-trial levels by day 19. The marked increase in Cr at day 5 was also reflected in the behaviour of concentrations of Se, and to a lesser extent As and V, though as with Cr, all of these oxyanionic species fell back to pre-treatment levels by the end of the trial at day 19. A slight fall in groundwater pH was noted post treatment, though at an average of 12.8, this was still very high.

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Figure 9: Rig used for soil mixing trial



Figure 10: Settlement of ground in area of plot following completion of soil mixing trial

## 6. GROUNDWATER MONITORING

A series of groundwater monitoring wells had previously been installed throughout the Shawfield site during 2007 and these were sampled again during 2011 and 2012 as part of a separate project. A number of these wells were located on the Shenkins site (Figure 1), of which BH47 is located hydraulically side gradient of the groundwater circulation trial, BH53 hydraulically downgradient of the direct injection trial and BH49 hydraulically

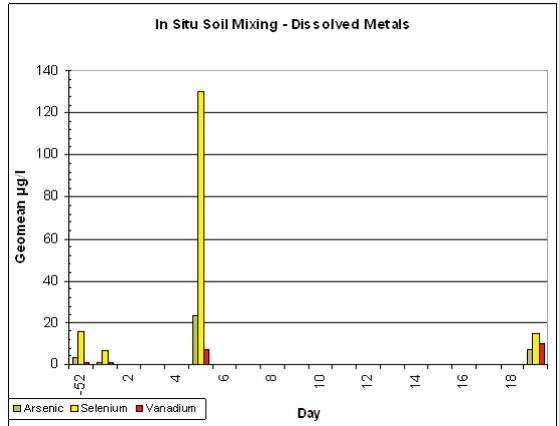
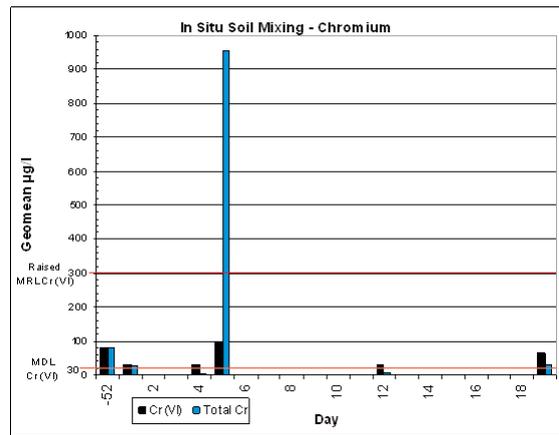


Figure 11: Concentrations of Total Cr, Cr(VI), As, Se and V prior to and following implementation of soil mixing trial

downgradient of the soil mixing trial. Four rounds of monitoring were undertaken during the pre-trial period of 2007/2008 and five to seven rounds (depending on well) commencing approximately two years after the trial in 2011, the most recent being in November 2012. Due to the range of Cr concentrations detected, the results are most easily represented on a log scale (Figure 12).

As BH47 is located side gradient of the re-circulation trial, it is not unexpected that little influence on groundwater concentrations was observed (especially given the severity of contamination in this area). In the case of BH53, Cr(VI) had

Table 4: Concentrations of total Cr, Cr(VI) and pH before and after soil mixing trial implementation

Matrix and analyte <sup>g</sup>	Unit	Pre-trial				Post trial <sup>a</sup>				Maximum		Stats. <sup>b</sup>	Sig. <sup>c</sup>	
		Mean	±	SD <sup>d</sup>	n <sup>e</sup>	Mean	±	SD	n	Pre-trial	Post-trial			
Soil	Total Cr	mg/kg	12,800	±	9451	14	9167	±	2130	6	41,000	13,000	WMW	Yes
Soil	Cr(VI)	mg/kg	342	±	466	14	<0.3	±	0.0	6	1300	0.3	WMW	Yes
Soil	pH		11.5	±	1.4	14	12.0	±	1.3	6	13	13	WMW	No
Leachate <sup>f</sup>	Total Cr	mg/kg	336	±	390	8	0.04	±	0.06	4	1200	0.1	WMW	Yes
Leachate	Cr(VI)	mg/kg	350	±	422	8	<0.3	±	0.0	4	1300	<0.3	WMW	Yes
Groundwater	Total Cr	µg/l	1025	±	1673	4	688	±	1516	5	3500	3400	WMW	Yes
Groundwater	Cr(VI)	µg/l	143	±	176	4	108	±	119	5	400	300	t	Yes
Groundwater	pH		12.8	±	0.0	4	12.2	±	0.2	5	13	12	t	No

f: as determined using a CEN 10: 1 leach test (BS EN 12457-2; 2002); g: Estimated analytical uncertainty: Cr(VI) in water 6.8%, total Cr in water 8.9%, Cr(VI) in soil 11.6%, total Cr in soil 6.5%

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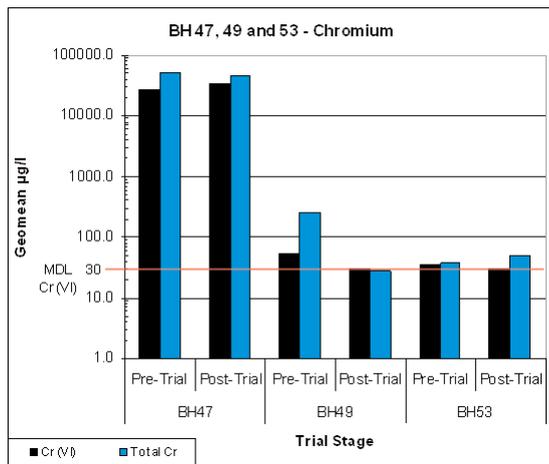


Figure 12: Concentrations of total Cr and Cr(VI) in the nearest site monitoring wells to the three trials showing the geometric mean of concentrations in 2007/2008 (pre-trial) and 2011/2012 (post trial)

only been detectable on one occasion previously and was not detectable post trial, though a slight increase in total Cr was observed in the post trial data. However, given the distance from the direct injection trial (60 m) the results may simply be reflective of contamination in the intervening area. On the other hand, BH49 which is located only 3 m downgradient from the soil mixing trial has returned non-detectable Cr(VI) as well as lower concentrations of total Cr, post application.

## 7. GENERAL DISCUSSION

There was a very high degree of heterogeneity in the material undergoing treatment, both across the Shenkins site as a whole and within each of the individual trial plots. All three trials provided confirmation of the effectiveness of CaSx in reducing Cr(VI), though it is clear that the degree of reduction obtained did vary according to the approaches used.

A comparison of the average percentage of Cr(VI) pre-trial and post trial in soil for the three approaches is summarised in Table 5.

Table 5: Cr(VI) as a % of total Cr in soil before and after treatment

Remedial approach	Cr(VI) as a % of total Cr in soil	
	Pre-trial	Post trial
Groundwater Re-circulation	2.45%	0.41%
Direct Injection	2.61%	0.02%
Soil Mixing	2.67%	<0.003%

The reductions in Cr(VI) obtained from the soils data need to be interpreted with caution. The pre and post trial analysis appeared to show that the soil mixing approach was more successful in terms of the degree of reduction obtained, through achieving non-detectable Cr(VI) post treatment.

However inspection of post treatment soils revealed the presence of what was assumed to be unreacted Cr(VI) in the form of bright yellow nodules, which typically constitute visual evidence of the oxidised metal (Figure 13). As such, the homogenisation process, which takes place during sample preparation in the laboratory may have the effect of bringing any unreacted CaSx into contact with residual particles of Cr(VI)-containing COPR.

Whilst there was lesser evidence of unreacted particles in the other trials, soils analysis supported their presence (albeit as relatively low level concentrations of



Figure 13: Presence of un-reacted Cr(VI) in soil sample on completion of soil mixing trial

Cr(VI). Furthermore, it is known that the alkaline digestion procedure (as used in the analytical methods, APHA/AWWA/WEF (1998) and US EPA Method 3060A (US EPA, 2007) may catalyse the reaction between CaSx and unreacted Cr(VI) (Wazne *et al.*, 2007), so the actual data may underestimate concentrations of residual Cr(VI) in soil.

The issue is of somewhat less concern at Shawfield on the basis that it is the groundwater concentrations of Cr(VI) that are the most critical issue and the aqueous analysis does not involve hot digestion. Notwithstanding the issues of raised reporting limits and data variability, all three trials achieved significant reductions in Cr(VI) to below 300 µg/l in groundwater. The reduction also appeared to be accompanied by limited mobilisation of the anionic species of metals, and where this was evident it appeared to be transient in nature. An increase in mobility followed by a decrease was also observed with some cationic metals (data not included) though in other cases these were below reporting limits.

All three trials appeared to have influence outside the specific area of application as observed in the peripheral monitoring wells. Breakthrough of CaSx was observed through colour changes in the groundwater in the monitoring wells outside the re-circulation trial area and in the changes in Cr(VI) and total Cr taking place within these wells. Similarly, daylighting of CaSx was observed in wells peripheral to the direct injection trial where changes in total Cr and Cr(VI) were also noted. Even with the soil mixing trial, changes in groundwater chemistry outside the plot were observed.

Both sulphur and calcium are significant components of the COPR residue and there was little difference in concentrations pre-trial or post trial in terms of calcium and sulphur species in soil (total sulphate concentrations typically in the 20,000-80,000 mg/kg range). In the groundwater, the mean sulphate concentration increased from 340 mg/l in the re-circulation trial to 13,000 mg/l at day 6 before falling back to 240 mg/l at 24 days. Free sulphur increased from a mean of 1.2 mg/l to 20 mg/l and 22 mg/l after 6 and 24 days respectively. The direct injection trial showed a substantial increase in sulphate content within groundwater from 69 mg/l to a mean of 17,480 mg/l after 24 days with free sulphur increasing from 0.05 mg/l to 10.4 mg/l, whilst there were lesser changes with soil mixing (4 mg/l to 7.4 mg/l for sulphate and 0.06 mg/l to 1.44 mg/l for free sulphur). Due to the high sulphate content of the soil it is not clear as to how much of the increases observed with re-circulation or direct injection are attributable to CaSx or to direct mobilisation. The subsequent decrease observed with the groundwater re-circulation trial, may also be the case with direct injection, though monitoring was terminated after day 20. In the longer term, mobility of sulphate will be reduced through formation of insoluble calcium sulphate.

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All three trials provided evidence of total Cr mobilisation as a combination of physical or chemical action. The soils showed a small but significant decrease in total Cr following treatment and there was some limited evidence of an increase in total Cr leachability following treatment. The soil mixing trial, which has the most aggressive action upon the soil structure, resulted in a spike of elevated chromium appearing in the groundwater at day 5. A key factor in the behaviour of Cr(III) at Shawfield is the elevated pH which promotes the formation of the more mobile  $\text{Cr}(\text{OH})_4^-$  species (Richard & Bourg, 1991), though this will be expected to precipitate as  $\text{Cr}(\text{OH})_3$  outside the source areas where treatment is taking place (comparison of the pH data does show some limited effect of the CaSx in raising the pH following application, though this will be countered by the buffering capacity outside of the area of application).

## 8. CONCLUSIONS

All three approaches for delivering CaSx have met with reasonable success, though practicability issues have a significant influence on technique selection within the context of the Shawfield site.

The re-circulation trial successfully reduced groundwater concentrations of Cr(VI) and has the advantage of not requiring full access to the area undergoing treatment. As was evident from the trial, however, the approach is vulnerable to precipitation of reactants or products (calcium, sulphur and chromium hydroxide) taking place within the formation and especially at the well interface. Such issues may be compounded by the likelihood of preferential flow channels within a complex substratum. The approach also requires a good understanding of hydrogeological conditions and whilst this is the case for the Shawfield site as a whole, it does not preclude local uncertainties associated with some of the infilled areas of COPR.

Soil mixing is a relatively efficient approach, (and is applicable both above and below the water table) though its reported success based on analytical data for soils has to be tempered with the appearance of unreacted nodules of Cr(VI), possibly resulting from a 'surface sealing' effect as a result of the rotary action. Nonetheless it achieved particularly effective reductions in Cr leachability and evidence from post remedial monitoring suggested that it has had a significant influence on groundwater concentrations of Cr hydraulically downgradient of the treatment area. However it requires completely free access to the area for treatment and will necessitate importation of material to address settling.

Direct injection is the most versatile of the three approaches and whilst more reliant on diffusion than the re-circulation trial, it appeared to be successful in achieving Cr(VI) reduction in groundwater. Whilst the other two approaches are not ruled out, it is considered likely that direct injection will represent the most appropriate way forward.

It is evident that groundwater concentrations of Cr(VI) can be reduced below 30  $\mu\text{g}/\text{l}$  (based on the direct injection trial). This is well below the Site Specific Action Criterion for the groundwater in the superficial deposits which has been identified as 521  $\mu\text{g}/\text{l}$  of total Cr, through quantitative risk assessment conducted by URS, on the assumption that pollutant linkages associated with local burns will be broken by engineering methods such as relining and re-aligning culverts.

It is noted that UK water quality guidelines are based on total chromium rather than Cr(VI), and whilst total Cr was also mostly reduced below this criterion in the trials, there is a potential for it to remain elevated as a result of the prevailing high pH conditions which may promote the mobility of Cr(III) as  $\text{Cr}(\text{OH})_4^-$ . However, the subsequent fall in pH outside the impacted areas would be expected to result in its conversion and precipitation to  $\text{Cr}(\text{OH})_3$ .

A treatment train approach, employing chemical reduction using CaSx, with a reliance on natural attenuation for subsequent Cr(III) mitigation is therefore anticipated to represent a key component of the overall remedial strategy. Integration of this approach with engineered containment both for the surface water courses discharging into the River Clyde and for soil contamination within the unsaturated zone is therefore viewed as a pragmatic solution to a historic industrial legacy and one that brings with it substantial benefits to the local economy.

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