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**Article** in *Land Contamination & Reclamation* · January 2010

DOI: 10.2462/09670513.984

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# Field application of calcium polysulphide for *ex situ* treatment of soils contaminated with chromite ore processing residue

Richard J.F. Bewley and Stuart Clarke

## Abstract

A field trial was undertaken to evaluate the application of calcium polysulphide (CaS<sub>x</sub>) for the treatment of hexavalent chromium (Cr(VI)) associated with chromite ore processing residue (COPR) deposited in south-east Glasgow, Scotland.

Various concentrations of 29% CaS<sub>x</sub> solution based upon 0.1×, 0.3×, 0.5× and 0.8× of the dosage that had achieved over 99% reduction in a laboratory trial were applied to skips containing approximately 4000 kg of material in conditions close to, or at, soil saturation.

Both the 0.5× and 0.8× dosages resulted in a reduction of Cr(VI) from mean starting concentrations of 742 and 822 mg/kg to below 2 mg/kg after 24 hours, with mean concentrations of 0.6–1.3 mg/kg remaining after 50 days. Leachable Cr(VI) (accounting for almost all the total Cr) was reduced from initial concentrations of 62–80 mg/L to 0.3 mg/L or below, following treatment. Dosages of 0.1× and 0.3×, or the 0.5× treatment under unsaturated conditions achieved a lesser degree of Cr(VI) reduction, although leachable Cr was still reduced to around 3 mg/L for the 0.3× application, and 0.6 mg/L for the 0.5× application in unsaturated soil.

Addition of CaS<sub>x</sub> did not generate detectable hydrogen sulphide and had little effect on concentrations of calcium or sulphide, although sulphate concentrations increased two- to three-fold.

In most treatments there were no significant differences in the mobility of other heavy metals following application. Increased leachability was observed in the case of selenium and vanadium, and to a lesser degree with mercury. However, such increases tended to be transient, at least for dosages up to and including the 0.5× application.

The findings demonstrate that CaS<sub>x</sub> represents a potentially viable treatment for Cr(VI) associated with the COPR deposited in the Glasgow conurbation.

Key words: calcium polysulphide, chromite, chromium, COPR, leachable, reduction

## INTRODUCTION

The south-east area of Glasgow, Scotland, was host to

one of the world's largest chromium plants that operated from the mid-nineteenth century until the late 1960s. Over this period it has been conservatively estimated that in the order of 1.5 million cubic metres of chromite ore processing residue (COPR) were deposited in various locations within an area of approximately 10 km<sup>2</sup>, much of this being used as infill material in former clay pits (CLAIRE 2007).

COPR is a geochemically complex material, but its environmental significance is driven by the occurrence

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Received February 2009; accepted May 2009

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of elevated concentrations of hexavalent chromium, Cr(VI) (Farmer *et al.* 2006). Unlike the trivalent form of chromium, which is of relatively low toxicity, Cr(VI) is classified by both the International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (USEPA) as a known human carcinogen, and hexavalent chromium compounds are also known to have mutagenic potential. Toxicity arising from Cr(VI) may occur via inhalation, ingestion or dermal exposure (DEFRA 2002).

During the early 1990s, elevated concentrations of Cr(VI) commonly in the hundreds or thousands of mg/kg were identified in 15 sites in the Rutherglen and Cambuslang areas of Glasgow, to depths of 10 m or greater (Bewley *et al.* 2001). Whilst in many instances the human exposure pathway was, or could be, mitigated by the presence of hardstanding, there were potential ongoing risks to groundwater, particularly through the presence of COPR within the saturated zone.

The chemical complexity of COPR militates against the application of many of the established treatments for Cr(VI) (Farmer *et al.* 2006; CLAIRE 2007), and a series of laboratory and field trials using both proprietary and non-proprietary techniques to treat Cr(VI) associated with COPR met with mixed success (Bewley *et al.* 2000). Microbiological techniques were hampered by the highly alkaline nature of the soil (typically in the pH 10 to 12 range), the need for further understanding of the mechanisms involved, and the difficulty in achieving microbial reduction throughout the mass of material undergoing treatment, especially in the unsaturated zone. Some promising results were obtained using physicochemical techniques, although a substantial proportion of unreacted Cr(VI) still remained.

A series of laboratory studies focusing on the nature of the COPR identified some of the factors contributing to the difficulty in achieving an appropriate degree of Cr(VI) reduction. This was partly as a result of the chemical complexity and availability of the Cr(VI) in the mineralogical phases within the COPR, where it occurred within hydrogarnet, hydrocalumite and ettringite. Addition of iron sulphate, one of the reducing agents used for conventional Cr(VI) treatment was of limited effectiveness due to the high pH of COPR causing the iron to precipitate and the release of Cr(VI)

from COPR through anion exchange of sulphate (Farmer *et al.* 2006).

Attention then began to focus upon the potential applicability of calcium polysulphide (CaSx) that had previously been employed in the treatment of Cr(VI) at sites in the USA (Fruchter *et al.* 2000), but had not, reportedly, been tested directly on COPR material.

Bench-scale experiments undertaken on samples of COPR taken from the Glasgow area indicated that CaSx was effective at reducing concentrations of Cr(VI) originally present at around 0.3 to 0.75% dry weight to insoluble Cr(III) (Graham *et al.* 2006). A stoichiometry of *c.* 5:1 for the active species in CaSx relative to Cr(VI) in the COPR material was effective over the pH range investigated, with Cr(VI) not being detected in either the equilibration solution (<0.01 mg/L) or the post-treatment solid phase (<10 mg/kg).

The reduction in Cr(VI) following treatment by CaSx did not appear to be accompanied by significant changes in mineralogical composition, although the occurrence of elemental sulphur was observed in nine of twelve treatments with CaSx.

The batch testing findings were supported by data from column leaching experiments, where <1% of the original Cr(VI) remained as Cr(VI) in the CaSx-treated column. Only *c.* 0.3% of the Cr(VI) was leached over the duration of the experiment. There was no evidence from the column that precipitation of either sulphur or chromium hydroxide resulted in any identifiable changes in permeability.

Modelling studies were undertaken in parallel with the experimental work. These were based on mineral solubility and the assumption of chemical equilibria between an assemblage of key mineral phases and a range of soluble aqueous species. The models predicted Cr(VI) concentrations in aqueous solutions and in the solution phase in equilibrium with the COPR, that were in reasonably good agreement with the experimental data.

In a later study relating to COPR in New Jersey, USA, a CaSx dosage of twice the molar stoichiometric requirement was reported to be sufficient to reduce Cr(VI) concentrations to below 2 mg/kg from starting concentrations above 100 mg/kg (Wazne *et al.* 2007). In a pilot-scale study involving treatment of 1000 kg of material with this same dosage of CaSx, approximately 62% of Cr(VI) was reduced after a curing period of ten

months, as measured using X-ray absorption near edge structure (XANES) spectroscopy.

Based upon the apparent success of the laboratory trials, it was therefore considered appropriate to conduct a field trial to evaluate the effects of CaSx for treatment of COPR-contaminated material from one of the Glasgow sites.

## MATERIALS AND METHODS

### Sourcing COPR-contaminated material

Material suitable for the trial had been identified at Rosebery Park, a former football ground located in Rutherglen, Glasgow, from which material had been collected during the previous bench-scale trials of CaSx (Graham *et al.* 2006).

Approximately 40 m<sup>3</sup> of material was collected from various locations within the site (typically from the upper 2 m) to create a stockpile that was mixed/turned using a JCB 3CX for approximately one hour to ensure that it was homogenized as thoroughly as possible. A series of eight ‘four-yard’ skips were then each filled with approximately 3 m<sup>3</sup> of material, five samples being collected from each one for chemical analysis of target analytes.

The skips were then transported to the treatment facility, where they were weighed, together with an empty skip to allow the weight of soil present in each one to be estimated. Each of the skips was then maintained under covered conditions using plastic sheeting throughout the duration of the trial in order to minimize rainfall infiltration.

### Treatment design

Previous bench-scale studies undertaken on samples of COPR derived from the Rosebery Park site had established that a stoichiometric ratio of *c.* 5:1 for the active species in CaSx relative to Cr(VI) was effective in reducing concentrations of Cr(VI) from starting concentrations of several thousand mg/kg, to below 10 mg/kg in the solid phase, and to below 0.01 mg/L in the equilibration solution (Graham *et al.* 2006).

Based upon information provided by the supplier of BSP CASCADE<sup>®</sup>, the commercial formulation of (29%) CaSx used in the trial (Best Sulfur Products, Fresno, CA), it was determined that a soil contaminated with 1000 mg/kg of Cr(VI) would require a dosage of approximately 100 mL of 29% CaSx/kg soil. Applica-

tions of CaSx were therefore referenced according to this concentration, referred to as the ‘design dosage’.

The field trial was undertaken in three phases, each phase proceeding a few days after the previous one.

Phase 1 was designed to investigate treatment of unsaturated soil, using applications of CaSx at 80% of (0.8×) and 50% of (0.5×) the design dosage. Following analyses of Cr(VI) in each skip-load of soil, the dosage of CaSx was apportioned according to the mean Cr(VI) concentration per skip. A control treatment was established using water only. Due to the differences in the material obtained for the field trial following on-site homogenization, the overall moisture content and water-holding capacity was not directly comparable to the relatively limited amount of material that was used in the bench-scale trial by Graham *et al.* (2006). Based on the latter, it had originally been intended to achieve unsaturated conditions within the soil; however, the amount of liquid applied using the 1× design dosage treatment (366 litres of 29% CaSx) would have raised the soil moisture content above saturation, so this was therefore limited to 300 litres (i.e. 0.8× the design dosage). In order to obtain comparable conditions, the equivalent percentage increase in liquid content (6.7 to 6.8% v/w) was achieved through adjusting the amount of water used to dilute the 0.5× treatment and for the control, which received water only.

Phase 2 was intended to investigate treatment of saturated soil, but, given the closeness of Phase 1 soils to saturation, it was decided to evaluate lower dosage treatments rather than attempt to simply replicate the Phase 1 treatments under full saturation. The applications of CaSx were dosed at approximately 30% (0.3×) and 10% (0.1×) of the design dosage (together with a water-only control) with sufficient water addition to attain a water capacity of around saturation (equivalent to a 7.1 to 7.3% v/w increase in liquid content).

Phase 3 was designed to examine conditions that were further below saturation than in Phase 1, by applying the 0.5× design dosage of CaSx, in order to raise the liquid content by 3.7 to 3.8% v/w. Two treatments were examined, one involving application of the CaSx and mixing as with the Phase 1 and Phase 2 trials (as described below), and the other involving a purely passive surface application, without any mixing.

The experimental design is summarized in Table 1.

**Table 1. Details of experimental design and liquid addition**

Phase		Phase 1			Phase 2			Phase 3
Name of treatment <sup>a</sup>		Control	0.5×	0.8×	Control	0.1×	0.3×	0.5× 'unsaturated'
Weight of soil tested	kg	3800	4420	4480	3620	4600	3280	4000
Theoretical amount of 29% CaSx to treat 1 kg of soil with 1000 mg/kg Cr(VI) at the 5:1 stoichiometric ratio	L	0.0995	0.0995	0.0995	0.0995	0.0995	0.0995	0.0995
Mean concentration of Cr(VI) in each skip load	mg/kg	944	742	822	706	864	974	828
Theoretical litres of 29% CaSx required (5:1 stoich.) for treating each particular skip load	L	357	326	366	254	395	318	330
Amount of water added in trial	L	260	150	0	254	285	154	0
Amount of CaSx added in trial	L	0	150	300	0	40	86	165
Total liquid addition (CaSx and water) in trial	L	260	300	300	254	325	240	150
△ Liquid addition (%v/w) <sup>b</sup>	%	6.8%	6.8%	6.7%	7.0%	7.1%	7.3%	3.8%
% of 'theoretical' CaSx addition <sup>a</sup>	%	0.0%	46.0%	81.9%	0.0%	10.0%	27.0%	45.5%

a. Treatment notation is based on the proportion of calcium polysulphide (CaSx) that had previously achieved a reduction of Cr(VI) from several thousands of mg/kg to below 10 mg/kg in the solid phase in bench-scale trials (Graham *et al.* 2006), referred to as the design dosage (stoichiometric ratio of c. 5:1 for the active species in CaSx, relative to Cr(VI)): i.e. 0.5× represents approximately 50% of the design dosage, 0.8×, approximately 80%, etc. The actual percentage of the design dosage is indicated in the bottom row.

b. This represents the increase in soil liquid content (expressed as %v/w) achieved through addition of the water and CaSx solution. Treatments were raised close to, or to full saturation in Phases 1 and 2 respectively, whereas Phase 3 remained unsaturated.

### Phase 1 and Phase 2 treatments

During the set-up of each treatment, approximately one-third of the material within the selected skip was transferred to a spare skip using a mini digger. Whilst this was being undertaken, water (in the case of the control) or an appropriate dilution of the stock 29% CaSx solution was prepared in an intermediate bulk container (IBC) located within the treatment area.

Once this initial aliquot of the material had been transferred, approximately one-third of the water or diluted CaSx solution was applied to it, using a petrol-powered pump, ensuring full coverage of the surface. A mini digger mixed the material and solution thoroughly to ensure that all material was in contact with the liquid. This process was repeated until all material had been transferred from the initial skip and all liquid had been added. The now-empty skip was used for the establishment of the next treatment. The potential for cross-contamination was minimized by establishing the control treatment first, and the pump, hose and IBC container were cleaned using water between the set-up of each treatment. A 50-mm diameter monitoring well, comprising a two-metre length of slotted pipe below the soil, connected to a one-metre length of plain pipe above it, and completed with a bung and gas tap, was

installed at an angle in the corner of each skip in order to facilitate gas monitoring.

Following completion of the set-up of each skip, soil, water and gas samples were collected at one, six and 13 days. At the 13-day sampling, duplicate soil samples were stored for 50 days by the laboratory prior to analysis in order to determine longer-term changes.

A predetermined number of soil samples (each one a composite of five sub-samples) were collected from each skip at the above time intervals. All sampling equipment, including the mini-digger bucket, was cleaned with water following completion of each sampling event.

Gas samples were also collected in Tedlar bags from the well-pipe installed in each skip at predetermined time intervals using a GA 2000 gas analyser (manufactured by Geotechnical Instruments, Leamington Spa, UK) as a pump.

### Phase 3 treatments

The Phase 3 unsaturated treatment was established similarly to the Phase 1 treatments, but without additional water added.

The undisturbed treatment was intended to assess the application of the CaSx solution without mixing.

As such, the CaSx solution was added directly to the surface of the material in the skip and allowed to naturally infiltrate the material. However, this resulted in the formation of a crust that impeded further permeation of the soil, so this treatment was subsequently abandoned.

### Chemical analysis

Soil and gas samples were transported in cooled containers under full chain-of-custody to the contract laboratory, Alcontrol Laboratories, for analysis.

The analyses performed on selected soil samples were undertaken according to in-house analytical methods (Alcontrol laboratories, pers. comm.). These were based on methods published by the American Public Health Association (APHA), the American Water Works Association (AWWA) and the Water Environment Federation (WEF), using a Kone Analyser for Cr(VI), total sulphate and sulphide, and using atomic absorption in the case of total mercury (APHA/AWWA/WEF 1999). The methods for other heavy metals and calcium were based on the United States Environmental Protection Agency (USEPA) methods 3050B, and 3060A for alkaline extraction of Cr(VI) from soil (USEPA 2007). Total sulphur was determined by combustion, based on the American Society for Testing and Materials (ASTM) Method D-1552 (ASTM 2003), and pH, according to the British Standards (BS) Method BS 1377: Part 3 (BSI 1990).

Leachable constituents were analysed using the NRA leach test (NRA 1994) with analysis of determinands as detailed above, apart from sulphur analysis by HPLC; mercury by cold vapour atomic fluorescence spectrometry, using British Standards method EN 13506 (BSI 2002b); and other metals by ICP-MS. Additional samples were subject to waste acceptance criteria ('WAC') testing, using a two-stage batch test according to British Standards method EN 12457-3 (BSI 2002a).

Each Tedlar bag was analysed for bulk gas composition, using an in-house method based on a method for methane and hydrogen gases published by the Department of the Environment (1988).

## RESULTS AND DISCUSSION

### Nature and properties of material used in trial

The material used in the trial essentially consisted of a mixture of chromium-contaminated soil and raw COPR from the same location, as would typically be encountered in any *ex situ* remedial work undertaken (Table 2). The properties of the material strongly reflected the COPR content, typified by total chromium concentrations in the order of 3500 mg/kg, of which almost 25% (*c.* 800 mg/kg) was present as Cr(VI), and which are within the general range encountered during previous investigations (Bewley *et al.* 2000, 2001). The material was highly alkaline, as indicated by an average pH of 9.8 and a calcium content of 6% w/w. Several heavy metals, including copper, zinc, lead, manganese, vanadium and selenium, were also present in concentrations typically in the low hundreds of mg/kg.

**Table 2. General characterization of material used in trial (pre-treatment)**

Soil parameter	Soil concentrations (mg/kg except for sulphur and pH)		
	Mean	± SD	<i>n</i>
Hexavalent chromium	836	± 122	40
Total chromium	3579	± 807	39
Total sulphate	3329	± 1252	17
Boron	3.5	± 0.0	17
Arsenic	28	± 10	17
Barium	225	± 43	17
Beryllium	0.8	± 0.7	17
Cadmium	0.4	± 0.1	17
Calcium	60 688	± 13 460	16
Copper	237	± 460	17
Iron	50 706	± 5452	17
Lead	258	± 145	17
Manganese	915	± 140	17
Mercury	0.7	± 0.1	17
Nickel	421	± 60	17
Selenium	3.0	± 0.0	17
Vanadium	234	± 32	17
Zinc	494	± 126	17
Sulphide (acid soluble)	<50		16
Sulphur (total as %)	0.21	± 0.04	17
pH	10	± 0.3	39

**Table 3. Effects of varying applications of CaSx on Cr(VI) concentrations in soil**

Phase	Treatment	Litres CaSx	Concentrations of Cr(VI) mg/kg											
			Day 0		Day 1	Day 6	Day 13	Day 50		Cr(VI) as % of total Cr				
			Mean	± SD	Mean	± SD	Mean	± SD	Mean		± SD			
1	Control	0	944 <sup>a</sup>	± 98	22	692 <sup>a</sup>	± 104	676 <sup>a</sup>	± 29	708 <sup>a</sup>	± 163	720 <sup>d</sup>	21	
	0.5×	150	742 <sup>a</sup>	± 56	23	1.9 <sup>a</sup>	± 0.9	1.1 <sup>a</sup>	± 0.3	1.3 <sup>a</sup>	± 0.5	1.3 <sup>c</sup>	± 0.1	0.04
	0.8×	300	822 <sup>a</sup>	± 113	23	1.3 <sup>a</sup>	± 0.9	0.7 <sup>b</sup>	± 0.3	0.5 <sup>a</sup>	± 0.3	0.5 <sup>c</sup>	± 0	0.02
2	Control	0	706 <sup>a</sup>	± 53	25	995 <sup>b</sup>	± 10	808 <sup>b</sup>	± 49	780 <sup>c</sup>	± 99	710 <sup>d</sup>	19	
	0.1×	40	864 <sup>a</sup>	± 100	25	243 <sup>b</sup>	± 26	165 <sup>b</sup>	± 13	170 <sup>c</sup>	± 0	160 <sup>c</sup>	± 0	4
	0.3×	86	974 <sup>a</sup>	± 159	26	76 <sup>b</sup>	± 36	55 <sup>b</sup>	± 84	33 <sup>c</sup>	± 2.1	27 <sup>c</sup>	± 4	0.80
3	0.5× unsat.	150	828 <sup>a</sup>	± 28	24	63 <sup>a</sup>	± 112	1.9 <sup>a</sup>	± 1.4	–	–	2.3 <sup>c</sup>	± 0.1	0.09

a. Mean of five samples; b. Mean of four samples; c = Mean of two samples; d = One sample collected  
– Not measured

### Effects of application of CaSx on Cr(VI) contamination

#### Soil concentrations

In the Phase 1 trial, both the dosage at 0.8× the design quantity and the 0.5× application resulted in a rapid reduction of Cr(VI), with mean starting concentrations of 742 and 822 mg/kg respectively being reduced to below 2 mg/kg after 24 hours (Table 3). This reduction was sustained throughout the following samplings undertaken, with both the 13- and 50-day samplings returning mean concentrations of 0.6 and 1.3 mg/kg for the 0.5× and 0.8× treatments. The Cr(VI) accounted for less than 0.05% of the total Cr present following application, as compared to 23% prior to treatment.

More moderate reductions in Cr(VI) were achieved with the lower concentrations of CaSx at 0.1 and 0.3× the design dosage, in Phase 2, with these stabilizing at around 100 and 30 mg/kg respectively. Nonetheless, these still represented losses of 80 to 95% Cr(VI), with the proportion of total Cr as Cr(VI) being reduced from around 25% to below 1 and 4% respectively.

In both the Phase 1 and Phase 2 controls, concentrations of Cr(VI) remained within the range of approximately 700 to 1000 mg/kg. The variations observed are likely to reflect the general heterogeneity of the material.

The Phase 1 and Phase 2 treatments were either close to, or at saturation, so the degree of contact throughout the soil matrix would be expected to facilitate the reduction process. This is evident from a comparison with the performance of the unsaturated 0.5× treatment applied in Phase 3, where a lesser degree of

reduction (though still in excess of 90%) had occurred after one day. By day 50, however, concentrations of Cr(VI) remaining were 2.3 mg/kg, i.e. less than 0.1% of the total Cr and comparable to the same treatment applied close to saturation, in Phase 1.

#### Leachate concentrations of chromium

The concentrations of total Cr and Cr(VI) present in the leachate generated from the material were relatively similar. Cr(VI) is known to be highly mobile under the alkaline conditions associated with COPR-impacted soil, as compared to Cr(III), which is of low solubility at these pH levels (Richard and Bourg 1991). The predominance of Cr(VI) over Cr(III) (as inferred by the difference between total Cr and Cr(VI) concentrations) is therefore to be expected.

For both the Phase 1 and Phase 2 treatments, the leachable concentration of both total and hexavalent chromium in the controls did not differ significantly over the course of the trial, remaining in the range of 50 to 70 mg/L (Table 4).

However, for the Phase 1 treatments, the leachable Cr(VI) from both the 0.8× and 0.5× treatments was reduced from initial mean concentrations of 62 mg/L and 80 mg/L to below 0.3 mg/L in each case. The 'unsaturated' treatment in Phase 3 also reduced concentrations substantially, these essentially being the same at day 6 (0.34 mg/L) and day 50 (0.32 mg/L).

For Phase 2, a lesser degree of reduction was observed with the 0.1× and 0.3× treatments, with the residual concentration of leachable Cr(VI) in the latter

**Table 4. Effects of varying applications of CaSx on total Cr and Cr(VI) concentrations in leachate**

Phase	Treatment	Litres CaSx	Total Cr in leachate (mg/L)									Cr(VI) in leachate (mg/L)								
			Day 0			Day 13			Day 50			Day 0			Day 13 <sup>a</sup>			Day 50		
			Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n
1	Control	0	67.5 ± 9.19	3	66.7 ± 13.2	3	55		1	70 ± 10	3	67 ± 13	3	58		1				
	0.5×	150	62.5 ± 4.95	3	0.001 ± 0	3	0.38 ± 0	2	62 ± 3	3	<0.03 <sup>b</sup>	3	0.26 ± 0.007	2						
	0.8×	300	70 ± 9.9	2	3.1	1	0.007 ± 0.002	2	80 ± 4	2	0.24 ± 0.18	3	<0.03	2						
2	Control	0	57.5 ± 4.95	2	51.5 ± 0.71	2	57		1	59 ± 4.9	2	56 ± 0.00	2	62		1				
	0.1×	40	72.5 ± 6.36	2	13.5 ± 0.71	2	14		1	75 ± 11	2	14 ± 0.71	2	16		1				
	0.3×	86	72 ± 2.83	2	2.5 ± 0.35	2	3.1		1	76 ± 5.0	2	2.6 ± 0.20	2	3.1		1				
3	0.5× unsat.	150	68 ± 4.24	2	0.72 <sup>a</sup> ± 0.021	3	0.56 ± 0.064	2	71 ± 1.4	2	0.34 ± 0.02	3	0.32 ± 0.03	2						

a. ×0.5 unsaturated treatment sampled on day 6  
 b. Below detection limit

**Table 5. Results of 'WAC' leach test for chromium (BS EN 12457-3)**

Phase	Treatment	Conc. in 2:1 eluate	Conc. in 8:1 eluate	2:1 conc. leached	Cumulative conc. leached	Limit values for compliance leaching test using BS EN 12457-3 at L/S 10 L/kg (mg/kg)		
		<sup>a</sup> C <sub>2</sub> mg/L	C <sub>8</sub> mg/L	A <sub>2</sub> mg/kg	A <sub>2-10</sub> mg/kg	Inert waste landfill	Stable non-reactive hazardous waste in non-hazardous landfill	Hazardous waste landfill
1	Control	210	63	420	840	0.5	10	70
2	0.1×	0.2	0.49	0.4	4.4	0.5	10	70
3	0.5× unsat.	1.2	1.8	2.3	17	0.5	10	70

a. Notation for each of the above as used in BS EN 12457-3

being an order of magnitude greater (3 mg/L) than the 0.5× treatment.

The Cr(VI) accounted for most of the total Cr concentrations in the leachate, both before and following treatment, apart from one single elevated concentration of total Cr at Day 13 for the 0.8× treatment (3.1 mg/L); however, as this was a single sample it may not necessarily be representative.

For convenience, the NRA method was used for leachate analysis, which provides a relatively conservative indication of the potentially mobile fraction of chromium present, as it involves full dispersion of the matrix. This method has been used here for broad comparisons of treatments. However, it is recognized that in current UK guidance, particularly in the area of waste compliance for landfilling purposes, the test has now been superseded by a cumulative two-stage batch test (BS EN 12457-3). As part of this current project, three (single) samples were taken for this testing from

each phase (the control treatment from Phase 1, the 0.1× treatment from Phase 2 and the 0.5× unsaturated treatment from Phase 3) at the end of the trial. The results for total chromium are presented in Table 5, which also includes the corresponding limit values for the three landfill types. The 8:1 eluate concentrations are broadly similar to the corresponding results from the NRA tests shown in Table 4, which reflects the broad similarity of the testing regime (the NRA test being based on a 10:1 water:soil ratio). The findings provide further confirmation of the reduction in mobility achieved by the application of CaSx, even at concentrations below the design quantity (0.1×). The greater reduction in leachability achieved by the latter, compared to the 0.5× unsaturated treatment, may reflect the greater degree of dispersion of the added CaSx, achieved in the saturated treatment. As indicated by the acceptance criteria presented in Table 5, this



does have implications if the material were to be disposed of by landfill.

The information on leachable Cr(VI) is of primary importance for evaluating the potential impact of any treated material on groundwater, and in this respect it is of greater importance than reduction in the solid phase alone. In terms of the latter, it has been suggested from longer-term studies undertaken by Wazne *et al.* (2007) and Moon *et al.* (2008), that the hot alkaline digestion process during the extraction applied to the soil samples could possibly accelerate the reaction between CaSx and any unreacted Cr(VI), thereby potentially overestimating its effects. Whilst this limitation to the Cr(VI) data in soils therefore needs to be clearly recognized, the data for the aqueous leachate samples (that were not subject to this digestion process as part of the analytical procedure) indicate that the reduction in Cr(VI) reported was consistent with the soil analysis. This is further reflected in the leachate data for the total Cr results and confirmed by reference to the BS EN 12457-3 leaching test.

**Changes in pH, calcium and sulphur compounds**

Soil pH, and concentrations of calcium and sulphur compounds have been compared against corresponding concentrations in each skip before and after treatment (Table 6). As a more limited number of samples were subjected to the leach test, it was considered appropriate to compare each of the post-treatment results against a ‘pooled’ mean concentration of the pre-treatment samples, given that the material had been sourced from the same location (Tables 6 and 7).

The application of CaSx did not result in pH changes of more than one unit. The 0.5x treatment in Phase 1 resulted in an increase in pH from 9.84 to 10.58, although no significant effects were observed when this was repeated under unsaturated conditions in Phase 3 (9.85 at the start compared to 9.52 at the end of the trial). For the highest dosage of CaSx, an increase from 10.13 to 10.73 was observed (Table 6).

Relatively elevated concentrations of calcium were present in the soil prior to treatment, so that the addition of CaSx had little significant effect either in terms of soil concentrations (Table 6) or concentrations in the leachate (Table 7), even for the highest dosage rate.

Increases in (acid-soluble) sulphide were not observed above the reporting limit, apart from the 0.8x treatment in the Phase 1 trial (Table 6) where one sam-

Table 6. Comparison of calcium, sulphur and sulphate content before and after treatment with CPS (50-day data shown)

	Control (Phase 1)				0.5x (100 litres) Phase 1				0.5x (100 litres) Phase 3 unsaturated				0.8x (300 litres) Phase 1				
	Pre-treatment soil concentrations		Conc. at end of trial		Pre-treatment soil concentrations		Conc. at end of trial		Pre-treatment soil concentrations		Conc. at end of trial		Pre-treatment soil concentrations		Conc. at end of trial		
	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
Total sulphate (mg/kg)	5300 ± 2828		2	2500	1	3033 ± 681	3	7650 ± 350	2	3150 ± 71	2	7400 ± 1414	2	3000 ± 781	3	10 300 ± 990	2
Total sulphur (%)	0.28 ± 0.06		2	0.23	1	0.23 ± 0.04	3	1.80 ± 0.10	2	0.21 ± 0.01	2	1.50 ± 0.00	2	0.17 ± 0.02	3	2.10 ± 0.21	2
Acid-soluble sulphide (mg/kg)	<50 ± 0		2	<50	1	<50	3	<250	2	<50	2	<50	2	<50	3	93 <sup>a</sup>	1
Calcium (mg/kg)	82 000 ± 21 213		2	55 000	1	55 333 ± 101 16	3	56 500 ± 500	2	56 000 ± 2828	2	51 500 ± 3536	2	67 000 ± 12 728	2	74 500 ± 19 092	2
pH	10.08 ± 0.40		5	10.20	1	9.84 ± 0.17	5	10.58 ± 0.01	2	9.85 ± 0.25	2	9.52 ± 0.14	2	10.13 ± 0.20	5	10.73 ± 0.07	2

<sup>a</sup> A second sample returned a value <250 mg/kg

Table 7. Comparison of leachability of key constituents before and after treatment with CPS

Analyte	Unit	Pre-treatment concentrations		Post-treatment with CPS (0.1x – Phase 2)		Post-treatment with CPS (0.3x – Phase 2)		Post-treatment with CPS (0.5x – Phase 1)		Post-treatment with CPS (0.5x – Phase 3)		Post-treatment with CPS (0.8x – Phase 1)	
		Mean (n=7)*	SD	Day 13	Day 50 <sup>d</sup>	Day 13	Day 50 <sup>d</sup>	Day 13	Day 50	Day 6	Day 50	Day 6	Day 50
Arsenic	µg/L	1.9 ± 0.9		2.0 ± 0.0	2.0	2.0 ± 0.0	2.0	4.5 ± 2.1	2 <sup>d</sup>	1.5 ± 0.7	1.5 ± 0.7	2.0 ± 0.00	
Barium	µg/L	20 ± 4.7		32 ± 0.7	130	62 ± 7.8	57	42 ± 0.7	37 ± 1.4	165 ± 7.1	49 ± 3.5	55 ± 3.5	
Beryllium	µg/L	<1		<1	<1	<1	<1	<1	<1	<1	<1	<1	
Boron	µg/L	<10		28 ± 2.1	<10	20 ± 3.5	<10	<10	<10	<10	115 ± 7.1	<10	
Cadmium	µg/L	<0.4		<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	
Calcium	µg/L	95 857 ± 13 359		75 000 ± 4243	77 000	71 500 ± 7778	65 000	84 500 ± 3536	71 500 ± 3536	99 500 ± 707	92 000 ± 5657	110 000 ± 14 142	
Copper	µg/L	7.4 ± 3.6		8.5 ± 2.1	11	10 ± 1.4	11	<1	4.5 ± 0.7	20 ± 1.4	21.5 ± 4.9	7 ± 2.8	
Iron	µg/L	8.0 ± 7.9		<5	<5	<5	<5	<5	<5	<5	<5	<5	
Lead	µg/L	5.1 ± 10		2.5 ± 2.1	<1	<1	<1	<1	<1	<1	13.5 ± 16.3	<1	
Manganese	µg/L	1.3 ± 0.5		<1	<1	<1	<1	<1	<1	<1	2.0 ± 0.0	<1	
Nickel	µg/L	<2		2.0 ± 0.00	3.0	2.0 ± 1.4	7.0	<1	2.0 ± 0.0	4.5 ± 2.1	7.0 ± 2.8	4 ± 1.4	
Selenium	µg/L	1.6 ± 0.8		2.5 ± 0.7	<1	5.5 ± 0.7	<1	41.0 ± 41.7	4 ± 3.5	1.0 ± 0.00	1.5 ± 0.7	21 ± 16.3	
Vanadium	µg/L	<1		<1	<1	<1	<1	11.0 ± 0.7	<1	<1	12.5 ± 3.5	10 ± 0.00	
Zinc	µg/L	24 ± 47		<3	8.0	<3	<3	5 ± 3	<3	10 ± 5.7	17 ± 0.00	<3	
Mercury	µg/L	<0.05 ± 0.0		<0.01	0.01	<0.01	<0.01	0.56 ± 0.6	<0.01	<0.01	<0.01	0.02 ± 0.01	
Sulphide	mg/L	<0.5 <sup>a</sup> ± 0.0		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Sulphate	mg/L	28 ± 31		40 ± 3.5	61	25 ± 0.00	30	14 ± 2	24.5 ± 0.7	26 ± 0.7	25 ± 0.7	22 ± 0.0	
Free sulphur	mg/L	<0.05		<0.05	<0.05	<0.05	<0.05	0.06 ± 0.0	<0.05	<0.05	<0.05	<0.05	
pH		8.82 <sup>b</sup> ± 0.3		10.48 ± 0.22	8.03	10.73 ± 0.09	10.52	11.16 <sup>c</sup> ± 0.15	8.62 ± 0.01	7.49 <sup>c</sup> ± 0.3	8.21 ± 0.05	8.55 ± 0.08	

\* Except as indicated: a = mean of four samples; b = mean of 15 samples; c = mean of three samples; d = one sample analysed

ple returned a concentration of 93 mg/kg after 50 days. There may also have been an increase in the case of the 0.5× dosage in Phase 1, as uncertainty exists due to the raised reporting limit, but post-treatment concentrations were still below 250 mg/kg. Additionally, the sulphide concentration remained below 50 mg/kg following treatment with the same dosage in Phase 3 under unsaturated conditions. Sulphide within the leachate was also consistently below reporting limits both pre and post treatment (Table 7).

Concentrations of total sulphur were in the 0.17 to 0.28% range prior to treatment. Following application of CaSx, these were raised to 1.8% for the Phase 1 0.5× treatment, 1.5% for the Phase 3 (unsaturated) 0.5× treatment and 2.1% for the for the Phase 1 0.8× treatment. Pre-treatment concentrations of free sulphur in the leachate were below the detection limit and in most cases remained close to, or below detection (<0.05 mg/l, Table 7), apart from a couple of samples receiving the 0.8× design dosage where 4 mg/L was leached at the 13-day sampling (data not shown). Nonetheless, by Day 50, this treatment, along with all others, returned leachate concentrations below detection (<0.05 mg/L).

A substantial increase was observed with sulphate following treatment (Table 6). The 0.8× design treatment and both the Phase 1 and Phase 3 treatments all had average starting concentrations of sulphate in the order of 3000 mg/kg, which increased to between 7400 and 10 000 mg/kg after 50 days. Sulphate formation is consistent with the oxidation of the CaSx through the reaction taking place, and was predicted by Graham *et al.* (2006). The data do, however, need to be viewed in the context of the variability associated with the material, as illustrated by the large standard deviation associated with the control treatment and the fact that the final result from the control was lower than the mean concentration at the start.

Interestingly, there was virtually no difference in concentrations of leachable sulphate before, during, or following the trial, as compared to the starting concentration, which averaged 28 mg/L: e.g. even with the 0.8× design dosage the mean concentration of leachable sulphate after 50 days was 22 mg/L (Table 7). The only exception to this was the treatment receiving the lowest concentration of CaSx (0.1× design dosage) where concentrations of 40 and 61 mg/L were reported after 13 and 50 days (Table 7), though this may just reflect the degree of variability in the material (particu-

larly in view of the large standard deviation associated with the control).

### Changes in heavy-metal mobility

In general, concentrations of heavy metals in the leachate constituted a relatively minor proportion of the total detected in the solid phase. Aside from Cr, concentrations of most of the heavy metals were detectable in the leachate at average concentrations of less than 10 µg/L, slightly higher in the case of zinc (Table 7).

Following treatment, concentrations of leachable heavy metals were broadly within the initial range of variability and no consistent trends were identified. In a few instances, most notably with selenium, vanadium and mercury, there was some limited evidence of an increase in mobility, but this was inconsistent across treatments, and, for mercury at least, appeared to be transient in nature. Conversely, concentrations of leachable zinc tended to show a decrease following treatment, although again, the pre-treatment samples demonstrated significant variability.

### Soil gas concentrations

There was little overall difference in soil gas concentrations between the treatments, with the key finding being that concentrations of hydrogen sulphide consistently remained below its detection limit (<1 ppm). Concentrations of carbon monoxide, carbon dioxide, hydrogen and methane were also less than their detection limits of <0.05%, 0.05% vol., 0.5% vol. and 0.05% vol. respectively.

## CONCLUSIONS

CaSx has been demonstrated to be an effective reductant for Cr(VI) associated with COPR-impacted soil within the concentration range examined in this study.

An application rate of approximately 150 litres of a 29% solution of CaSx/4000 kg of soil contaminated with 700 to 800 mg/kg Cr(VI) achieved a reduction in Cr(VI) concentrations to 1 to 2 mg/kg, representing a percentage reduction in the order of 99.5% or greater. Applications of this dosage also reduced potentially leachable Cr(VI) from approximately 70 mg/L to around 0.2 mg/L. A higher dosage resulted in an even greater reduction in leachable Cr(VI) to below the detection limit.

The addition of CaSx does not appear to be accompanied by any significant permanent changes in the mobility of other heavy metals, apart from a limited degree of elevation of selenium and vanadium, although even these both appear to decrease with time. A slight increase in mercury above the detection limit was noted, but this too appeared transitory, decreasing to around the detection limit or below detection after a few days.

On this basis it is therefore considered that CaSx represents a promising treatment for Cr(VI) associated with COPR. No gross changes in volume were visually observed from the trial, and previous research by Graham *et al.* (2006) has indicated limited changes in mineralogical properties, so this appears to be encouraging from the standpoint of 'heave' potential. The latter issue will, however, need to be explored further before the appropriateness of full-scale application can be confirmed. For unsaturated material, an active treatment approach, involving mixing of CaSx into the mass of material undergoing treatment also appears to be advantageous, to avoid the potential impediment posed by crust formation.

An *ex situ* approach as described in this trial may therefore have applicability in the treatment of relatively localized sources of contamination that can be relatively easily accessed and treated potentially in batch mode. The treatment could be applicable as a stand-alone solution, or potentially as a pre-treatment prior to landfill disposal. One possible application would be within a 'soil hospital' or hub site to which material is brought for treatment, were this to be considered as a viable option.

The most significant area of concern with respect to COPR-derived contamination relates to the risks to controlled waters and in particular the presence of such contamination below the water table, as an ongoing source. The performance of CaSx *in situ* and the most effective means of its delivery to the sub-surface therefore represent the next stage of evaluation.

## ACKNOWLEDGEMENTS

The project was undertaken for Glasgow City Council, to whom thanks are expressed for permission to publish this paper and particularly to Mr Simon Watson for his support. We also thank I & H Brown for undertaking the engineering works, Hitech Equipment Limited for

providing a site for conducting the trial and Alcontrol Laboratories for conducting the chemical analysis.

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