



***In Situ* Remediation of Chromium in Soil and Groundwater**

ReSolution Partners, LLC, 967 Jonathon Drive, Madison, WI 53713

INTRODUCTION

A chrome-plating facility in the Midwestern United States was situated over 3 m of silt which overlay 24 m of sand and gravel. The sand and gravel supported an unconfined aquifer with a water table ~ 2 to 3 metres below the ground surface. Historical releases of chromium from plating operations active from 1942 to 1995 resulted in a 900 metre-long plume of hexavalent chromium (Cr^{6+}) as a result of leaching to groundwater flowing beneath the site. Concentrations of Cr^{6+} in the groundwater were as high as 160 mg/L. An interim groundwater pump and treat system was started in December 1995 to stop the continued migration of chromium beyond the facility property line. Chromium was removed from the pumped water using ion-exchange resins and the water discharged to a nearby creek. Regenerant from the exchange columns were sent off-site for management as hazardous waste.

The plating building was demolished in March 1996, with debris sent to hazardous and solid waste landfills (\$1,270,000US including engineering). This allowed access to soil that contained to a maximum of 7,500 mg/kg of Cr^{6+} (40 investigation samples). Maximum total chromium concentrations were as high as 39,000 mg/kg. Approximately 6,200 tonnes of soil would be classified as hazardous waste if excavated.

The contaminated soil was a continuing source of Cr^{6+} contamination to the groundwater. Numerical modeling of chromium leaching to groundwater indicated that the leachable Cr^{6+} from the soil should be less than 2 mg/L in order to achieve a chromium concentration of <0.10 mg/L in the top of the aquifer. A total of 5,800 m³ of soil to depths of ~3 m beneath the plating building area was targeted for remediation.

TREATMENT DESIGN

The remediation plan called for the in situ treatment of the chromium to convert the Cr^{6+} to Cr^{3+} . In the +3 oxidation state the chromium is rendered practically insoluble (lower mobility) and nontoxic (lower risk). An iron-based remedy using ferrous sulphate/ferric chloride was selected to form $\text{Cr}_{0.25}\text{Fe}_{0.75}(\text{OH})_3$ (Palmer and Wittbrodt, 1991). This mineral phase lowers chromium solubility to <0.10 mg/L at pH's as low as ~4.5 range. The shallow soil setting was expected to remain aerobic, supporting the stability of chromium by this approach.

Laboratory treatability studies were used to confirm the chromium sequestration when leached by simulated acid rain (USEPA SW-846, Method 1312). These studies found that 6 weight percent ferrous sulphate would produce a 99 percent reduction of leachable Cr^{6+} in the naturally alkaline soil. Reducing the soil pH to <7 improved the process to a 99.99 percent concentration reduction. Ferric chloride was used to reduce the pH and add more ferric iron to the soil for chromium-iron mineral formation.

IMPLEMENTATION

Dry reagents were supplied in 0.9-tonne sacks. The site was divided into grids and the required reagent dose was applied to the grid. A tracked excavator and a MITU-12 soil mixing machine were used to mix the ferrous and ferric iron reagent to the soil at 6 and 3 weight percent, respectively.

Mixing and stabilization performance were tested with grab samples collected from each grid volume for in-field analysis of Cr⁶⁺. Final determination of remediation performance to meet regulatory agency requirements was defined by a grid of 26 vertically-composited soil samples submitted to a certified laboratory for chromium analyses. Once the stabilization was determined to be complete, the area was paved and supported the sale of the site for continuing site manufacturing operations.

RESULTS

Figure 1 illustrates the performance of chromium stabilization in the soil as a cumulative probability plot. Concentrations of Cr⁶⁺ in the 26 regulatory agency defined grids ranged from 3 to 2,500 mg/kg (median of 67 mg/kg). Grid samples collected after the stabilization was thought to be complete included four grids with relatively high Cr⁶⁺ concentrations (5 to 1,300 mg/kg, median of 1.9 mg/kg). These four grids were retreated and retested to yield the final results with maximum and median concentrations of 5.3 mg/kg and 1.4 mg/kg, respectively. Fifty percent of the final results were less than the 1.3 mg/kg laboratory reporting limit and the overall Cr⁶⁺ reduction in soil was 99.4 percent.

Figure 2 illustrates the response of groundwater concentrations to the soil stabilization in two representative monitoring wells immediately downgradient of the plating facility. These wells showed 500- to 650-fold Cr⁶⁺ concentration decreases. All but well GW-4 decreased below the 0.10 mg/L remediation target. Hydrologic evaluation suggested that seasonal increases in water table elevation likely encountered a small pocket of unstabilized soil immediately above the water table that is periodically exposed to groundwater leaching. The regulatory agency did not require additional soil remediation.

The *in situ* remedy cost ~\$1,300,000 including subgrade foundation demolition, grading, paving, engineering support and documentation. The *in situ* remedy saved an estimated \$500,000 over excavation and off-site disposal as solid or hazardous waste. The groundwater containment system collected 847 kg of chromium before the soil stabilization (annual regenerant disposal cost of ~\$260,000 US). Three years after soil remediation the containment system collected only 21 kg chromium per year. The containment system was subsequently shut down.

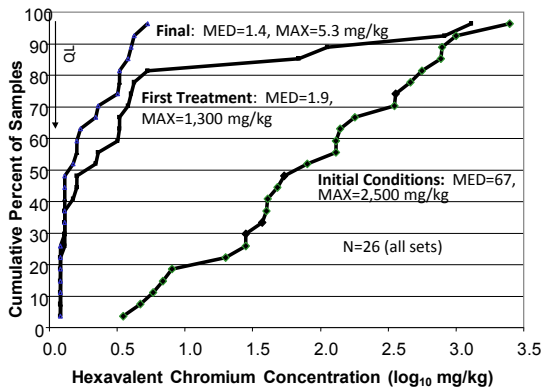


Figure 1. Cr⁶⁺ concentration reductions in soil.

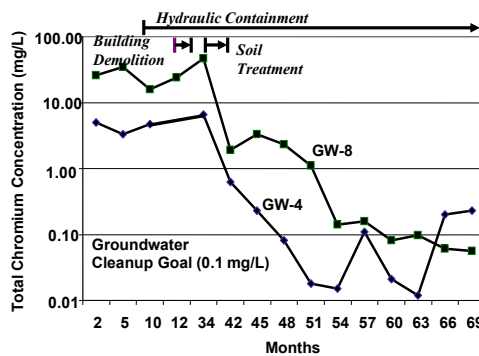


Figure 2. Total Cr concentration reductions in groundwater.



REFERENCES

Palmer, C. D. And P. R. Wittbrodt (1991). Processes affecting the remediation of chromium-contaminated sites. *Environmental Health Perspectives*, 92:25-40.

Safety Data Sheet

1. IDENTIFICATION OF THE MATERIAL AND SUPPLIER

Product Name: FERROUS SULFATE HEPTAHYDRATE

Other name(s): Ferrous sulphate heptahydrate; Iron sulphate heptahydrate; Iron sulfate heptahydrate; Iron protosulfate; Irosul.

Recommended use of the chemical and restrictions on use: Water and sewage treatment; reducing agent; wood preservative; fertiliser; chemical manufacture.

Supplier: Orica Australia Pty Ltd
ABN: 99 004 117 828
Street Address: 1 Nicholson Street,
Melbourne 3000
Australia

Telephone Number: +61 3 9665 7111
Facsimile: +61 3 9665 7937
Emergency Telephone: 1 800 033 111 (ALL HOURS)

2. HAZARDS IDENTIFICATION

Not classified as Dangerous Goods by the criteria of the Australian Dangerous Goods Code (ADG Code) for transport by Road and Rail; NON-DANGEROUS GOODS.

Classified as hazardous according to the Globally Harmonised System (GHS) of Classification and Labelling of Chemicals; HAZARDOUS SUBSTANCE.

Classification of the substance or mixture:

Acute toxicity - oral - Category 4
Skin corrosion/irritation - Category 2
Serious eye damage/eye irritation - Category 2A
Long-term hazards to the aquatic environment - Category 4

SIGNAL WORD: WARNING



Hazard Statement(s):

H302 Harmful if swallowed. H315 Causes skin irritation. H319 Causes serious eye irritation. H433 Harmful to terrestrial vertebrates.

Precautionary Statement(s):

Prevention:

P102 Keep out of reach of children. P264 Wash hands thoroughly after handling. P270 Do not eat, drink or smoke when using this product. P280 Wear protective gloves/protective clothing/eye protection/face protection. P273 Avoid release to the environment.

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Response:

P301+P312 IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell. P330 Rinse mouth. P302+P352 IF ON SKIN: Wash with plenty of soap and water. P321 Specific treatment (see First Aid Measures on this Safety Data Sheet). P332+P313 If skin irritation occurs: Get medical advice/attention. P363 Wash contaminated clothing before re-use. P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. P337+P313 If eye irritation persists: Get medical advice/attention.

Disposal:

P501 Dispose of contents/container in accordance with local/regional/national/international regulations.

Poisons Schedule (SUSMP): None allocated.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Components	CAS Number	Proportion	Hazard Codes
Iron(II) sulfate, heptahydrate	7782-63-0	>=98%	H302 H319 H315

4. FIRST AID MEASURES

For advice, contact a Poisons Information Centre (e.g. phone Australia 131 126; New Zealand 0800 764 766) or a doctor.

Inhalation:

Remove victim from area of exposure - avoid becoming a casualty. Seek medical advice if effects persist.

Skin Contact:

If skin or hair contact occurs, immediately remove any contaminated clothing and wash skin and hair thoroughly with running water. If swelling, redness, blistering or irritation occurs seek medical assistance.

Eye Contact:

If in eyes, hold eyelids apart and flush the eye continuously with running water. Continue flushing until advised to stop by a Poisons Information Centre or a doctor, or for at least 15 minutes.

Ingestion:

Rinse mouth with water. If swallowed, do NOT induce vomiting. Give a glass of water. Never give anything by the mouth to an unconscious patient. Seek immediate medical assistance.

Indication of immediate medical attention and special treatment needed:

Treat symptomatically.

5. FIRE FIGHTING MEASURES

Suitable Extinguishing Media:

Not combustible, however, if material is involved in a fire use: Extinguishing media appropriate to surrounding fire conditions.

Specific hazards arising from the substance or mixture:

Non-combustible material.

Special protective equipment and precautions for fire-fighters:

Decomposes on heating emitting toxic fumes, including those of oxides of sulfur. Fire fighters to wear self-contained breathing apparatus and suitable protective clothing if risk of exposure to products of decomposition.

6. ACCIDENTAL RELEASE MEASURES

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Emergency procedures/Environmental precautions:

Clear area of all unprotected personnel. If contamination of sewers or waterways has occurred advise local emergency services.

Personal precautions/Protective equipment/Methods and materials for containment and cleaning up:

Wear protective equipment to prevent skin and eye contact and breathing in dust. Work up wind or increase ventilation. Cover with damp absorbent (inert material, sand or soil). Sweep or vacuum up, but avoid generating dust. Collect and seal in properly labelled containers or drums for disposal. Wash area down with excess water.

7. HANDLING AND STORAGE

Precautions for safe handling:

Avoid skin and eye contact and breathing in dust.

Conditions for safe storage, including any incompatibilities:

Store in a cool, dry, well ventilated place and out of direct sunlight. Do not store above 24°C. Store away from incompatible materials described in Section 10. Keep containers closed when not in use - check regularly for spills.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Control Parameters: No value assigned for this specific material by the National Occupational Health and Safety Commission. However, Exposure Standard(s) for constituent(s):

Iron salts, soluble (as Fe): 8hr TWA = 1 mg/m³

As published by Safe Work Australia Workplace Exposure Standards for Airborne Contaminants.

TWA - The time-weighted average airborne concentration of a particular substance when calculated over an eight-hour working day, for a five-day working week.

These Workplace Exposure Standards are guides to be used in the control of occupational health hazards. All atmospheric contamination should be kept to as low a level as is workable. These workplace exposure standards should not be used as fine dividing lines between safe and dangerous concentrations of chemicals. They are not a measure of relative toxicity.

Appropriate engineering controls:

Ensure ventilation is adequate and that air concentrations of components are controlled below quoted Workplace Exposure Standards. Avoid generating and breathing in dusts. Use with local exhaust ventilation or while wearing dust mask. Keep containers closed when not in use.

Individual protection measures, such as Personal Protective Equipment (PPE):

The selection of PPE is dependant on a detailed risk assessment. The risk assessment should consider the work situation, the physical form of the chemical, the handling methods, and environmental factors.

Orica Personal Protection Guide No. 1, 1998: F - OVERALLS, SAFETY SHOES, CHEMICAL GOGGLES, GLOVES, DUST MASK.



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Wear overalls, chemical goggles and impervious gloves. If dust exists, wear dust mask/particulate respirator meeting the requirements of AS/NZS 1715 and AS/NZS 1716. Always wash hands before smoking, eating, drinking or using the toilet. Wash contaminated clothing and other protective equipment before storage or re-use.

9. PHYSICAL AND CHEMICAL PROPERTIES

Physical state:	Solid
Colour:	Light Grey to Off-white or White
Odour:	Odourless
Molecular Formula:	FeSO ₄ · 7H ₂ O
Solubility:	Soluble in water.
Specific Gravity:	1.898 (water = 1)
Relative Vapour Density (air=1):	Not available
Vapour Pressure (20 °C):	Not available
Flash Point (°C):	Not applicable
Flammability Limits (%):	Not applicable
Autoignition Temperature (°C):	Not available
Melting Point/Range (°C):	64
pH:	3.7 (10% solution)

10. STABILITY AND REACTIVITY

Reactivity: Hygroscopic: absorbs moisture or water from surrounding air.
Chemical stability: Stable.

Possibility of hazardous reactions: Hazardous polymerisation will not occur.

Conditions to avoid: Avoid dust generation. Avoid exposure to moisture. Avoid exposure to air.

Incompatible materials: Incompatible with alkalis, oxidising agents, soluble carbonates, gold and silver salts, lead acetate, lime water, potassium, potassium iodide, sodium tartrate, sodium borate, tannin, vegetable astringent infusions and decoctions.

Hazardous decomposition products: Oxides of sulfur.

11. TOXICOLOGICAL INFORMATION

No adverse health effects expected if the product is handled in accordance with this Safety Data Sheet and the product label. Symptoms or effects that may arise if the product is mishandled and overexposure occurs are:

Ingestion: Swallowing can result in nausea, vomiting, diarrhoea, and gastrointestinal irritation. Symptoms of swallowing large amounts of soluble iron compounds may be delayed several hours and can include epigastric pain, vomiting blood and circulatory failure. (1)

Eye contact: An eye irritant.

Skin contact: Contact with skin will result in irritation.

Inhalation: Breathing in dust may result in respiratory irritation.

Long Term Effects: Evidence indicates that repeated or prolonged exposure to this chemical could result in effects on the liver. (1)

Toxicological Data:

Product Name: FERROUS SULFATE HEPTAHYDRATE
Substance No: 000031011301

Issued: 12/09/2012
Version: 4

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Oral LD50 (rat): 319 mg/kg. (2)

Respiratory or skin sensitisation: No information available.
Germ cell mutagenicity: No information available.
Carcinogenicity: No information available.
Reproductive toxicity: No information available.
Specific Target Organ Toxicity (STOT) - single exposure: No information available.
Specific Target Organ Toxicity (STOT) - repeated exposure: No information available.
Aspiration hazard: No information available.

12. ECOLOGICAL INFORMATION

Ecotoxicity Avoid contaminating waterways.

13. DISPOSAL CONSIDERATIONS

Disposal methods:

Refer to local government authority for disposal recommendations. Dispose of material through a licensed waste contractor. Normally suitable for disposal at approved land waste site.

14. TRANSPORT INFORMATION

Road and Rail Transport

Not classified as Dangerous Goods by the criteria of the Australian Dangerous Goods Code (ADG Code) for transport by Road and Rail; NON-DANGEROUS GOODS.

Marine Transport

Not classified as Dangerous Goods by the criteria of the International Maritime Dangerous Goods Code (IMDG Code) for transport by sea; NON-DANGEROUS GOODS.

Air Transport

Not classified as Dangerous Goods by the criteria of the International Air Transport Association (IATA) Dangerous Goods Regulations for transport by air; NON-DANGEROUS GOODS.

15. REGULATORY INFORMATION

Classification:

Classified as hazardous according to the Globally Harmonised System (GHS) of Classification and Labelling of Chemicals; HAZARDOUS SUBSTANCE.

Classification of the substance or mixture:

Acute toxicity - oral - Category 4
Skin corrosion/irritation - Category 2
Serious eye damage/eye irritation - Category 2A
Long-term hazards to the aquatic environment - Category 4

Hazard Statement(s):

H302 Harmful if swallowed. H315 Causes skin irritation. H319 Causes serious eye irritation. H433 Harmful to terrestrial vertebrates.

Poisons Schedule (SUSMP): None allocated.

This material is listed on the Australian Inventory of Chemical Substances (AICS).

Product Name: FERROUS SULFATE HEPTAHYDRATE
Substance No: 000031011301

Issued: 12/09/2012
Version: 4

Safety Data Sheet



16. OTHER INFORMATION

- (1) In 'Martindale - The Extra Pharmacopoeia. 29th Edition. Ed. Reynolds J. The Pharmaceutical Press, London, 1989.'
(2) Canadian Centre for Occupational Health and Safety - Web Info Service. 2002.

This safety data sheet has been prepared by Orica SDS Services.

Reason(s) for Issue:

5 Yearly Revised Primary SDS
Addition/Change of synonymous name(s)
Product name change

This SDS summarises to our best knowledge at the date of issue, the chemical health and safety hazards of the material and general guidance on how to safely handle the material in the workplace. Since Orica Limited cannot anticipate or control the conditions under which the product may be used, each user must, prior to usage, assess and control the risks arising from its use of the material.

If clarification or further information is needed, the user should contact their Orica representative or Orica Limited at the contact details on page 1.

Orica Limited's responsibility for the material as sold is subject to the terms and conditions of sale, a copy of which is available upon request.



Source Area Soil Treatability Study Summary – Indiana Plating Facility

ReSolution Partners, LLC, 967 Jonathon Drive, Madison, WI 53713

Sample Selection

A total of five soil samples were prepared for this treatability study evaluation of a former plating facility: four composite samples with various concentrations of Cr^{6+} , and two samples with Ni. The following samples collected during the Phase 2 site investigation were composited for the Cr^{6+} evaluation.

- Composite 1: B-34 (0-4'), B-35 (0-4'), B-41 (0-4'), and B-30 (0-4')
- Composite 2: B-35 (4-8'), B-37 (4-8'), B-34 (4-8'), and B-30 (4-8')
- Composite 3: B-34 (12-16'), B-41 (12-16'), and B-37 (12-16')
- Composite 4: B-35 (16-20'), B-36 (16-20')

Composite 1 contained higher Cr^{6+} concentrations near the surface with soil described as organic silt and clay. Composite 2 consisted of fine sand with some silt. Composites 3 and 4 were fine sand with some silt and gravel.

The Composite 1 sample also contained subsamples with higher detected Ni concentrations based on laboratory results. Composite 1 was used for the Ni stabilization evaluation. Sample B-30 (16-20') was tested for leachable nickel, but the concentration was too low to carry forward into the stabilization trials.

Baseline Testing

Baseline testing included a screening Toxicity Characteristic Leaching Procedure (TCLP) on the four composite samples for Cr^{6+} to verify if the material required management as a hazardous waste. The TCLP-chromium concentrations were below the Toxicity Characteristic (TC) level of 5.0 mg/L. In addition, data suggest that some of the Cr^{6+} is reduced by the TCLP leaching solution to trivalent chromium, which is precipitating out of the solution.

Since Ni is not a RCRA managed waste and Cr^{6+} was below the TC requirement, all samples were subjected to the Synthetic Precipitation Leaching Procedure (SPLP) to evaluate the leaching potential of the material to the underlying groundwater in an *in situ* remediation application.

Attachment 1 provides a summary of the baseline test results.

Treatment Trials

Soil Amendment Reduces Hexavalent Chromium Contamination

Chrome Shop, Former Better Brite Metal Plating Facility

De Pere, Wisconsin

In August 1999, RMT, Inc. conducted ROD soil stabilization work at the Better Brite Plating Company Zinc and Chrome Shops Superfund site in De Pere, Wisconsin, EPA ID: WIT560010118. The primary contaminant of concern at the site was hexavalent chromium; secondarily, trivalent chromium and zinc were also contaminants of concern. Previous remedial activities onsite had included groundwater treatment, implemented in 1990, and soil surficial removal, conducted in 1993. Soil stabilization work was completed in November 1999 and the EPA Preliminary Closure Report was issued February 2000.

To alleviate direct contact and inhalation exposure dangers to public health, investigatory work at the Chrome Shop source-area identified 15,000 cubic yards of soil were impacted by hexavalent chromium. The selected remedy was soil treatment via chemical reductant, EnviroBlend®. Soil was stabilized *in-situ* by mixing the amendment into soils, targeting a maximum depth of twenty feet below ground surface – the bottom extent of hexavalent chromium impact.

Chemical amendment and mixing was conducted in two foot lifts. Amendment application used various pieces of construction equipment to distribute the material over the excavation area. A rototiller attachment on the end of an equipment boom conducted soil mixing. Post-treatment, confirmatory soil samples were subjected to Synthetic Precipitation Leaching Procedure (SPLP) testing; soils were then excavated and stockpiled onsite. Confirmatory testing showed the final treatment resulted in hexavalent chromium levels of less than ten micrograms per liter.

After achieving the specified twenty-foot mark for *in-situ* treatment, treated soils were replaced in the excavation, compacted, and a layer of clean fill, approximately one-half-foot in thickness, was deposited on top of the compacted soils. Drainage and erosion control elements, including buildings, asphalt, and vegetative cover were added post-compaction and -grading. Permitting restrictions were implemented post-construction phase, including land use and well drilling and groundwater use, both municipal and private.

Information obtained from Wisconsin Department of Natural Resource, Northeast Region and U.S. EPA Region 5 – Better Brite Plating Company Chrome and Zinc Shops ROD and closure report, with assistance from RMT, Inc.



Based on the baseline results, multiple dosage rates of ferrous sulfate and a pH amendment were added to the samples, and then tested to measure SPLP reductions. The four composite samples were initially tested for Cr^{6+} reduction using ferrous sulfate. All four composite samples were reduced to <0.01 mg/L with a 1% dose of ferrous sulfate.

On April 2, 2013, following the completion of the chromium trials, the consultant provided the results from the Ni Phase 2 Investigation field samples. Based on those results, Composite 1 and sample B-30 (16-20') were analyzed for untreated SPLP-Ni. Composite 1 had a significantly higher leachable Ni concentration than B-30, and was used for additional trials to evaluate stabilization performance.

The sample was first dosed with ferrous sulfate at the levels consistent with those that reduced chromium leaching. The ferrous sulfate reduced the pH of the SPLP leachate, which resulted in increasing the leaching of the nickel from 0.49 to 2.7 mg/L. Applying a dosage rate of 1% magnesium oxide to the 1% ferrous sulfate dose increased the pH and decreased the nickel concentration to 0.15 mg/L. However, with the increased pH, the Cr^{6+} concentrations in Composite 1 also increased from <0.010 to 0.39 mg/L. This was still a 90 percent reduction in the untreated sample, which leached 3.7 mg/L of Cr^{6+} . It is clear that the remedy will have to balance the sequestration of Cr^{6+} with some degree of pH buffering to optimize the reduction in leaching of both Ni and Cr^{6+} . Additional chemistry optimization can be performed after a determination is made on the remediation goals for the site.

Soil Sample	Formulation (wt %)		Soil pH	Pretest TCLP pH	Leaching Solution	Final Leaching pH	Chromium VI			Nickel		
	Ferrous Sulfate	Magnesium Oxide					TCLP (mg/L)	SPLP (mg/L)	Percent Reduction	Total	SPLP (mg/L)	Percent Reduction
Remediation Goals								to be determined			0.3	
B-30 (16'-20')	untreated				SPLP E	9.10				9.7	0.009	
Composite TS-1	untreated		8.14	2.37	TCLP 1	5.12	2.6					
	untreated				SPLP E	8.46		3.7		20	0.49	
	1.0	--			SPLP E	6.47		<0.010	> 99.73		0.94	-91.8
	3.0	--			SPLP E	4.76		<0.010	> 99.73		2.7	-449.0
	5.0	--			SPLP E	4.50		<0.010	> 99.73			
	1.0	1.0			SPLP E	9.54		0.39	89.5		0.15	69.4
Certified Sample analyzed by PACE								0.46	87.6		0.11	77.6
Composite TS-2	untreated		8.30	6.66	TCLP 2	5.67	0.025					
	untreated				SPLP E	9.35		0.46				
	1.0	--			SPLP E	7.17		<0.010	> 97.83			
Composite TS-3	untreated		8.32	6.78	TCLP 2	5.71	1.8					
	untreated				SPLP E	9.35		2.7				
	1.0	--			SPLP E	7.18		<0.010	> 99.64			
Composite TS-4	untreated		8.38	6.88	TCLP 2	5.76	0.56					
	untreated				SPLP E	9.42		0.87				
	1.0	--			SPLP E	7.12		<0.010	> 98.85			