Demonstration of SILVER II for the decontamination and destruction of organics in transuranic waste (Phase 1)

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Decontamination/Destruction Technology Demonstration for Organics in Transuranic Waste

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ABSTRACT

The United States Department of Energy's Savannah River Site has approximately 5000 55-gallon drums of ^{238}Pu contaminated waste in interim storage. These may not be shipped to WIPP in TRUPACT-II containers due to the high rate of hydrogen production resulting from the radiolysis of the organic content of the drums. In order to circumvent this problem, the ^{238}Pu needs to be separated from the organics – either by mineralization of the latter or by decontamination by a chemical separation.

We have conducted "cold" optimization trials and surrogate tests in which a combination of a mediated electrochemical oxidation process (SILVER IITM) and ultrasonic mixing have been used to decontaminate the surrogate waste materials. The surrogate wastes were impregnated with copper oxalate for plutonium dioxide. Our process combines both mineralization of reactive components (such cellulose, rubber, and oil) and surface decontamination of less reactive materials such as polyethylene, polystyrene and polyvinylchloride. By using this combination of SILVER II and ultrasonic mixing, we have achieved 100% current efficiency for the destruction of the reactive components.

We have demonstrated that:

- The degree of decontamination achieved would be adequate to meet both WIPP waste acceptance criteria and TRUPACT II packaging and shipping requirements
- The system can maintain near absolute containment of the surrogate radionuclides
- Only minimal pre-treatment (coarse shredding) and minimal waste sorting are required
- The system requires minimal off gas control processes and monitoring instrumentation
- The laboratory trials have developed information that can be used for scale-up purposes
- The process does not produce dioxins and furans
- Disposal routes for secondary process arisings have already been demonstrated in other programs

Based on the results from Phase 1, the recommendation is to proceed to Phase 2 and use the equipment at Savannah River Site to demonstrate the processing of genuine plutonium contaminated wastes.

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1 Introduction

1.1 BACKGROUND

Scope of the Problem

The United States Department of Energy's Savannah River Site, near Aiken, South Carolina has approximately 5,000 55-gallon drums of ^{238}Pu contaminated waste in interim storage. Due to the high rate of hydrogen production resulting from the radiolysis of the organic content of the drums, these cannot be shipped to WIPP in TRUPACT-II containers. In order to circumvent this problem, the ^{238}Pu needs to be separated from the organics – either by mineralization of the latter or by decontamination by chemical separation.

The USDOE has structured an evaluation program for potential treatment technologies in four phases. Phase I is a cold test on a simulant waste to demonstrate the basic technology. Phase II is a hot test using genuine waste material for technologies relying on decontamination. Phase III is a $>1/5$ th scale demonstration selected from technologies successful at Phase I/II, while Phase IV is the equivalent hot demonstration. AEA Technology is offering its SILVER IITM technology for evaluation operating as a partial mineralization combined with decontamination.

Program Objectives

The goal of this program was to reduce the ^{238}Pu content of this fraction by a factor of about 100, so that the radiolytic hydrogen production will be within WIPP requirements for use of the TRUPACT-II transport container.

SILVER II Summary

AEA Technology's patented SILVER IITM process has been developed to mineralize a broad range of organic wastes at low temperatures and pressures. Initial work in the 1980's was directed towards the treatment of radioactive contaminated organic wastes – comprising solvents, PUREX extractants, ion-exchange resins, cellulosic tissues, and polymeric materials. The organic components of the waste were converted to carbon dioxide and water, which could be safely discharged into the environment, leaving a minimal volume of radioactive residues for immobilization before storage and then disposal. In addition, it is able to dissolve plutonium and uranium oxides into nitric acid solution through a mediated catalytic oxidation. Therefore, it is ideally placed to treat combustible or mixed plutonium contaminated wastes, as a way of removing organic material from the waste and segregating the plutonium.

SILVER II has already been demonstrated to mineralize cellulose organic material, ion exchange resins and oil to carbon dioxide and water and to decontaminate the surface of polymeric materials, which due to their lower surface area react more slowly. Most metals will dissolve in the SILVER II medium – including mild steel, stainless steel, tin copper, lead, cadmium, mercury. Other materials for example: ceramics, platinum and glass will not dissolve, but any plutonium contaminating the surface will. In this way, some of the waste

material will either be mineralized or dissolved – while the remainder will be decontaminated wherever the surfaces can be contacted with the SILVER II solution.

A SILVER II impurity management system can be used to:

- Extract dissolved materials
- Recover the silver catalyst and nitric acid for recycling.
- Neutralize metal salts for subsequent immobilization of a waste form containing little organic material.

If desired, the Pu content could be separated for recovery. The residues of ceramic/glass plus undissolved organic polymer (principally PVC) can be washed in decontaminated streams recycled internally within the SILVER II process prior to separate immobilization.

At the heart of the SILVER II process is the chemical oxidation of organic molecules by the Ag(II) ion. This is one of the most oxidizing species that can be generated at an anode in an electrochemical cell in aqueous solution. Radical species, initiated by Ag(II), attack the organic substrate, progressively converting it irreversibly to carbon dioxide, water and residual salts. During each oxidation step, Ag(II) is reduced back to Ag(I). This is then regenerated to Ag(II) at the electrochemical anode. This 'catalytic' use of silver makes this a Mediated Electrochemical Oxidation Process. The organic species do not have to be water-soluble to be successfully treated by SILVER II, as has been shown by the successful treatment of solvents, oils, ion-exchange resins, tissues etc. The effect on comminuted PE and PVC under organic oxidation conditions (60-90°C) is to produce a surface decontamination effect rather than destruction.

Dissolved PuO₂ is retained in the aqueous phase. Any aerosols can be eliminated by condensation and HEPA filtration. The non-transuranic wastes arising from the process comprise carbon dioxide, carbon monoxide and water from the mineralized organic waste. These can be discharged in the gas phase to atmosphere after condensation and filtration. Any nitrogen oxide arisings can be scrubbed post HEPA-filtration. The rate of organics oxidation increases as the temperature is raised.

SILVER II Benefits

The advantages of the SILVER II process are that:

- i) it operates at low temperature (20-90°C) – thus avoiding the risk of any dioxins and furans.
- ii) it operates at atmospheric pressure - minimizing the risk of leakage.
- iii) the applied cell current directly controls the rate of reaction. On interruption, the reaction stops - thus acting as a fail-safe.

The SILVER II process does not produce the toxic or carcinogenic discharges associated with incineration (including dioxins, furans, polyaromatic hydrocarbons).

SILVER II Process Issues

The key to achieving Decontamination Factors >100 is related to giving access of the solution to the contaminating particulates. Much of the actual SRS waste of interest is enclosed in bags, and these will need to be penetrated to allow contact with the SILVER II solution. A number of options have been demonstrated as part of other waste treatment

programs – including shredding and cryogenic size reduction and a report on the options available has been issued to the customer¹.

Waste Composition

From the mean composition of SRS drummed ²³⁸Pu waste prepared by SRS, 45% by mass falls within the cellulose/resin/rubber category. As a 55-gallon drum contents of lightly packed material of this nature has been determined to weigh 25kg, this equates to a daily throughput of 11kg. A 4kW SILVER II plant (a single FM21 electrolytic cell) can process more than 10kg of cellulosic waste in a 24-hour period – i.e. virtually 1 drum/day. The remaining 55% of waste mass (as polymer sheeting, ceramics and metals) will appear in the low-level transuranic waste stream - corresponding to ~25 liters before immobilization.

The drum contents consist of heterogeneous job control waste primarily contaminated with ²³⁸PuO₂. The drum is lined with a polyvinylchloride liner. Waste is placed in the drum in four to six layers of polyvinylchloride bags. Drums may contain numerous waste bags. Waste contents include polyvinylchloride, cellulose, metals, and other job control waste, and may contain cans and bottles (both metal and plastic) containing hazardous liquids.

Any of the following regulated contaminants may be present in the actual wastes.

- Acids and bases may exist either as dried residue or as liquid trapped in containers – hydrochloric acid, nitric acid, sulfuric acid, and caustic soda
- Chlorinated hydrocarbon solvents would not be expected to be above the parts per million range in the air space, however, they could be present in the liquid form trapped in containers (bottles, cans) – carbon tetrachloride, chloroform, perchloroethylene, trichloroethylene, etc.
- Combustibles may exist as liquids trapped in containers - acetone, isopropyl alcohol, and methanol
- Radionuclides of concern in the actual wastes include primarily sub-micron ²³⁸PuO₂ particles. Trace amounts of other transuranics may also be present (plutonium-239, plutonium-241, etc.)
- Toxic metals would be present in the solid form such as cadmium coated materials, chromium coated materials, lead coated materials, leaded gloves (lead shot in rubber gloves), mercury coated materials, and mercury thermometers

1.2 OBJECTIVES

The following paragraphs, which have extracted from the proposal request document provide an outline of the US DOE's approach and objectives for this Phase I effort.

Phase I – Proof of Principle Cold Demonstration - Approach

The Offeror will plan and conduct a Proof of Principle Cold Demonstration at the Offeror's Facility. The phase will demonstrate, on a non-radioactive surrogate matrix (cold demonstration), an oxidation destruction, a reduction destruction, or a decontamination process for the organic materials in radioactive heterogeneous debris at the Savannah River Site. The cold demonstration of the oxidation/reduction technology should prove the effectiveness of the proposed technology to destroy organic constituents in a non-radioactive surrogate heterogeneous debris waste matrix that includes hazardous constituents. The cold

¹ 20 3067 01 07 Phase I Feed Preparation

demonstration of the decontamination technology should prove the process viability and safety prior to proceeding to Phase II (decontamination proof of principle demonstration with real radioactive waste). The process must accomplish this task without emitting undesirable products in the off gas. This includes off gas from the primary treatment unit to the atmospheric protection and control system, and effluents from the atmospheric protection system, by eliminating the conditions that lead to *de novo* synthesis of dioxins and furans in the atmospheric protection system.

Phase I – Proof of Principle Cold Demonstration – Requirements

The process shall be designed to meet these requirements:

- The system shall produce no dioxins and furans
- The system shall be able to maintain near absolute containment of radionuclides
- The system shall require minimal pre-treatment (sorting, size reduction, shredding) of the waste stream
- The system shall produce waste forms that meet the Waste Isolation Pilot Plant Waste Acceptance Criteria
- The system shall produce waste forms that meet the TRUPACT-II packaging and shipping requirements
- The system shall demonstrate disposal paths for any secondary non-transuranic waste generated by the process
- The system shall require minimal off gas control processes and monitoring instruments
- For decontamination systems -The system shall attain a minimal decontamination factor of 100

The report details how each of these objectives has been achieved.

2 Executive Summary

Background

The United States Department of Energy's Savannah River Site has approximately 5000 55-gallon drums of ^{238}Pu contaminated waste in interim storage. These may not be shipped to WIPP in TRUPACT-II containers due to the high rate of hydrogen production resulting from the radiolysis of the organic content of the drums. In order to circumvent this problem, the ^{238}Pu needs to be separated from the organics – either by mineralization of the latter or by decontamination through a chemical separation.

The customer supplied surrogate waste samples contaminated with copper oxalate to represent the plutonium oxide.

Results

Under Phase I of this contract, AEA Technology has demonstrated that the combination of its patented SILVER II technology incorporating ultrasonics is an effective and safe method of achieving this decontamination with DFs of 64 being recorded. This is an excellent result especially since no sample pre-treatment (such as the proposed shredding process) was adopted. The surrogate waste was treated as supplied.

Specifically, this work has demonstrated that:

- Irrespective of the form of the 'waste', it is possible to recover copper from all of the sample types that are expected in the real waste. The process performs both mineralization and surface-decontamination (>98% copper recovery)
- Inclusion of pre-treatment processes, such as coarse shredding, will increase these levels of 'decontamination'
- The action of 'decontamination' was controlled mainly by the rate of dissolution and was enhanced by using the ultrasonic/SILVER II combination
- A 'sweep' mode of ultrasonic agitation was more effective than a 'static' mode. The ultrasonic frequency is varied in sweep mode to provide a means for moving the ultrasonic action (nodes) through the entire volume of the anolyte vessel.
- Cellulosic materials and nylon were readily mineralized with a current efficiency of 100%. The attack on bulk polythene, neoprene and PVC was slower - thus giving a surface decontamination effect. The rate of attack on neoprene increased with both temperature and ultrasonic power
- Higher temperature and ultrasonic power resulted in increased bulk organic attrition that is beneficial if the material concerned contains contamination deep within the organic matrix

The work completed has provided:

- The design and fabrication of a small-scale plant that can be shipped to SRS under Phase II of the project and used there for the demonstration and treatment of actual SRS wastes
- Optimized process parameters for surrogate SRS waste streams

The work has also demonstrated that DFs of 64 are readily achievable on waste streams similar to those being stored at SRS.

The positive results obtained in Phase I of this project confirm that the combination of SILVER II with ultrasonics is an extremely effective decontamination technology for plutonium-contaminated organics. Indeed, the combined approach was shown to be successful for the decontamination of 'soft substrates' (such as rubber) which hitherto had proved to be resistant to decontamination using SILVER II alone. This is a major advancement.

In addition, as SILVER II is known to readily dissolve PuO_2 at 20°C and the rate of release of the copper oxalate surrogate has shown to be dominated by its slow dissolution rate, it is very likely that the genuine waste in Phase II will be easier to treat than the surrogate used in Phase I. As a result, increased DFs are expected during these active trials and this will achieve the goal of segregating ^{238}Pu from residual un-mineralized organics.

Test Set-up

The demonstration test system comprised a titanium ultrasonic vessel that was used to store the waste samples in the anolyte solution. A 60-amp electrochemical cell was used to generate the Ag(II) . The solution containing the Ag(II) was recirculated continuously through the anolyte vessel.

Tests 1-7 were optimization trials and the waste comprised masking tape, neoprene with rubber cement, PVC tape, glass frits, epoxy-coated polythene bottle, polythene bag with Vaseline, polystyrene weigh boat with RTV (an organic cement), glass with PVC coating and neoprene with glue - all were contaminated with copper oxalate as a surrogate. A handiwipe, paper towel and a nylon bag were also included in this waste.

The wastes in tests 8 (and 10) comprised a cork-occluded Tygon tube, epoxy-coated (internal) polythene bottle, PVC-coated glass vial with pump oil, and a polythene bag with PVC tape and pump oil - all copper oxalate contaminated. Other items included HEPA filter, weigh pan, paper towel, nylon bag, 'oil dry', and an atomic swipe.

The wastes in tests 9 comprised a TBP-soaked rubber glove, an oil-soaked rubber glove, masking tape on metal, weigh pan and wooden mixing stick with Vaseline, and a polythene bottle with PVC tape - all copper oxalate contaminated. Other items included a Hypalon-Neoprene composite and a nylon bag.

3 Experimental

The operation of the plant is given in document 'SRS SILVER II – System Manual' that has already been issued to the customer². In brief the plant consists of three main elements.

3.1 SILVER II UNIT

The equipment is operated inside a fume cupboard.

The Anolyte Circuit

- The anolyte vessel is a heated 5-liter titanium vessel (PV1) fitted with ultrasonic transducers. The transducers agitate the vessel contents so that the surfaces are constantly washed with Ag(II) bearing anolyte solution
- Circulation pump (P1) for pumping anolyte through the electrochemical cell to regenerate Ag(II) ions
- Anolyte off gas condenser (PV3) to condense vapors from anolyte vessel to prevent losses
- Soap film meter (PV5) to measure off gas flow rate
- Instrumentation to measure liquid flow and anolyte temperature
- Connecting pipework and valves made from PVDF

The Catholyte Circuit

- Glass 5-litre catholyte vessel (PV2)
- Circulation pump (P2) for pumping catholyte through the electrochemical cell.
- Catholyte off gas condenser (PV4) to condense vapors from catholyte vessel to prevent losses
- Instrumentation to measure liquid flow
- Connecting pipework and valves made from PVDF

Electrochemical cell

The cell is made from a matrix of ceramic membranes, PVDF spacers, electrodes and seals sandwiched between steel end plates.

A variable power supply (20V DC 60 A) is provided to power the electrochemical cell.

² 20 3067 01 12 SRS SILVER II Plant Manual

Figure 1 Photograph of the SRS SILVERII unit in a fume hood

3.2 TEST PLAN

The specified test plan was agreed with staff from SRTC and was devised to provide sufficient data to meet the objectives as described in the SOW. Nine laboratory-scale tests were to be conducted during the Phase I program. The cold tests comprised:

- A matrix of tests (#1-7), each of 8-hour duration, to determine the effect of temperature and agitation (ultrasound) as a function of exposure time. The tests were operated at different temperatures and agitation conditions - including no agitation - using a PVC/rubber/cellulose mixtures. The objective of these tests was to determine the conditions to be used for 2 final tests using revised surrogates with agreement on these conditions from SRTC.
- Using the best conditions identified in test 1 to 7, two further tests were conducted, one each using the full simulant waste compositions specified as Surrogate 1 and Surrogate 2. The objective was to achieve mineralization of cellulose and a DF > 100 for other materials when treated in combination. The total component weights for each surrogate had been calculated to achieve objectives within an experimental run duration of 8 hours

These are described below and summarized in Table 1.

Table 1 Test Outline

Test	Material	Temp / deg C	Ultrasound / Watt	Duration / h	Analyses
1	PVC/rubber/cellulose	60	None	8	Cu every 2 hours in anolyte + EOR in catholyte & on solid, TOC in anolyte/catholyte SOR/EOR
2	PVC/rubber/cellulose	60	100	8	
3	PVC/rubber/cellulose	80	200	8	
4	PVC/rubber/cellulose	45	100	8	
5	PVC/rubber/cellulose	80	None	8	
6	PVC/rubber/cellulose	60	150	8	
7	PVC/rubber/cellulose	60	150 Sweep	8	
8	Surrogate 1	60	150 Sweep	8	Cu every 2 hours in soln + EOR on solids, TOC every 2 hours in soln
9	Surrogate 2	60	150 Sweep	8	
10 ³	Surrogate 1a	60	150 Sweep		

The objective is to provide a process that can both destroy reactive organic components, such as cellulose based materials, as well as decontaminate the surfaces of unreactive components (such as PVC and PE). Complete organic destruction is not desirable since this will increase the plant size. From the results of the scoping trials, it was decided that the conditions that fulfilled this objective were:

- Run at 60C
- Operate with 150W swept ultrasonics
- Expect RTV and epoxy to be recalcitrant and the performance to be poor if the solution cannot access the contaminated surface

³ Test 10 was an extra test. During testing, we concluded that the eighth run (first surrogate sample) should be extended and that a tenth run (using a duplicate of the first surrogate sample) should be performed. These actions were agreed with staff from SRTC.

3.3 SAMPLES FOR TESTING

SRTC Staff provided the samples for both parametric testing and surrogate testing. The compositions of these waste samples are provided in Table 3 to Table 7. A photograph of a typical sample is provided in Figure 2. The samples can be subdivided into groups (Table 2). It should be noted that the samples comprising contamination enclosed within some form of organic cement (RTV, epoxy, rubber glue) would not be present under real operating conditions. These materials were selected since they had proved extremely recalcitrant during tests with other decontamination techniques, so were included to establish an upper limit on the decontamination technology?

Table 2 Samples description

Type	Parametric samples 1-7	Surrogate sample 8	Surrogate sample 9
Organics	<u>Masking tape</u> <u>Neoprene & bubbler with rubber cement*</u> <u>PVC tape</u> Handiwipe Paper towel Nylon bag <u>PS weigh pan with RTV*</u> <u>PE bottle with epoxy</u> <u>PE bag with Vaseline</u> <u>Neoprene with glue</u>	<u>PE bag with PVC tape and pump oil</u> <u>Tygon with 2 corks and TBP</u> Weigh pan Handiwipe Paper towel <u>PE bottle with epoxy and stick*</u> Nylon bag Oil dry Atomic swipe	Hypalon-Neoprene <u>Rubber glove with TBP</u> <u>Rubber glove with oil</u> <u>PE bottle with PVC tape</u> Nylon bag
Inorganic	<u>Filter frits</u>	<u>Glass with PVC coating</u> <u>Vial with pump oil*</u> HEPA filters	
Mixed	<u>Glass with PVC coating</u>		<u>Weigh pan with stick & Vaseline & metal fittings</u> <u>Metal tube with masking tape</u>
<u>Underlined samples</u> are those that have been contaminated with copper oxalate * samples contain some form of encapsulated copper oxalate, using RTV sealant or epoxy glue or rubber cement			

Table 3 Parametric test samples 1-3, the materials are broken down by weight in grams.

Materials	Substrate 1	Substrate 2	Copper Oxalate	Cu	Substrate 1	Substrate 2	Copper Oxalate	Cu	Substrate 1	Substrate 2	Copper Oxalate	Cu
	Sample #1				Sample #2				Sample #3			
Masking tape	2.585		0.069		2.781		0.0653		2.3651		0.0594	
Neoprene & bubbler with rubber cement**	6.8164	1.4636	0.0572		7.2949	1.7451	0.0569		6.9556	1.4244	0.0544	
PVC tape	4.2651		0.0587		4.0156		0.0576		4.1575		0.0581	
Handiwipe	3.8191				3.875				3.7918			
Paper towel	2.351				2.3867				2.3608			
Filter frits			0.0445				0.0453				0.0408	
PE bottle with epoxy	3.4014	3.297	0.0319		3.5301	1.5463	0.0353		3.5552	1.4384	0.0332	
PE bag with Vaseline	2.5883	1.1807	0.0662		2.5967	1.2572	0.054		2.4748	1.0001	0.0562	
Nylon bag	7.6				7.3				7.5			
PS weigh pan with RTV	1.9752	1.1931	0.0548		1.9944	1.0341	0.0547		2.0649	1.1113	0.0546	
Glass with PVC coating	83.8207	0.7468	0.1029		83.3013	0.7808	0.1035		83.1103	0.7043	0.1023	
Neoprene with glue	7.3053	0.0447	0.0339	0.5191	7.4723	0.0605	0.035	0.5076	7.2935	0.0158	0.0332	0.4922

** Note: Bubbler weight not included in substrate weight; rubber cement weight reflects wet weight

Table 4 Parametric test samples 4-6, the materials are broken down by weight in grams.

Materials	Substrate 1	Substrate 2	Copper Oxalate	Cu	Substrate 1	Substrate 2	Copper Oxalate	Cu	Substrate 1	Substrate 2	Copper Oxalate	Cu
	Sample #4				Sample #5				Sample #6			
Masking tape	2.6934		0.058		2.2033		0.0623		2.4626		0.0672	
Neoprene & bubbler with rubber cement**	6.881	1.989	0.0605		7.0431	1.2969	0.0592		7.5565	1.4135	0.0543	
PVC tape	4.1418		0.0569		4.2455		0.0551		4.4377		0.0573	
Handiwipe	3.6639				3.5804				3.5345			
Paper towel	2.3703				2.356				2.3671			
Filter frits			0.0442				0.0426				0.0432	
PE bottle with epoxy	3.2726	1.5623	0.0329		3.3614	1.8538	0.033		3.37	1.8218	0.0351	
PE bag with Vaseline	2.6849	1.2267	0.0542		2.3961	0.7962	0.0608		2.6371	1.5902	0.0541	
Nylon bag	7.7				7.8				7.5			
PS weigh pan with RTV	1.9536	1.0079	0.0549		1.9193	1.1346	0.0572		1.9345	1.114	0.0563	
Glass with PVC coating	85.4537	0.5749	0.103		84.0867	0.7076	0.1044		83.8447	0.7433	0.1016	
Neoprene with glue	7.2928	0.0554	0.031	0.4956	7.3303	0.0671	0.0339	0.5085	7.1893	0.0446	0.0339	0.503

** Note: Bubbler weight not included in substrate weight; rubber cement weight reflects wet weight

Table 5 Parametric test sample 7, the materials are broken down by weight in grams.

Materials	Substrate 1	Substrate 2	Copper Oxalate	Cu
	Sample #7			
Masking tape	2.5695		0.0658	
Neoprene & bubbler with rubber cement**	7.3312	1.2788	0.0583	
PVC tape	4.3602		0.0656	
Handiwipe	3.7307			
Paper towel	2.3705			
Filter frits			0.0409	
PE bottle with epoxy	3.5183	1.9709	0.0349	
PE bag with Vaseline	2.6763	0.7989	0.0552	
Nylon bag	7.6			
PS weigh pan with RTV	1.9847	1.4538	0.0574	
Glass with PVC coating	83.7821	0.7358	0.1016	
Neoprene with glue	7.2167	0.0478	0.0339	0.5136

** Note: Bubbler weight not included in substrate weight; rubber cement weight reflects wet weight

Table 6 Surrogate test sample 8 and test sample 10 (Surrogate 1A and 1B), the materials are broken down by weight in grams.

Material	Substrate 1	Substrate 2	Substrate 3	Copper Oxalate	Copper	Substrate 1	Substrate 2	Substrate 3	Copper Oxalate	Copper
	Sample #1A					Sample #1B				
HEPA filters	1.0282					1.0772				
Tygon with 2 corks and TBP	9.6229	0.4746	0.7876	0.0232		9.1788	0.4809	0.7382	0.0297	
Weigh pan	1.9528					1.6691				
Handiwipe	1.9335					1.8397				
Paper towel	2.4294					2.4155				
PE bottle with epoxy and stick	6.3074	2.9195	1.3021	0.019		6.219	2.642	1.4312	0.0195	
Nylon bag	6.3					6.4				
Glass with PVC coating	5.5759	0.5472		0.0259		5.6345	0.3538		0.0229	
Oil dry	3.3674					3.3687				
Vial with pump oil*	12.1435	0.5069		0.0253		12.1171	0.5069		0.0233	
Atomic swipe	3.773					3.6033				
PE bag with PVC tape and pump oil**	2.1856	1.4991	0.8134	0.0369	0.1303	2.295	1.4352	0.8288	0.0416	0.137

* Note: Oil baked in furnace to degradation

** Note: Copper in this matrix is both in the oil (27.4%) and under the tape

Table 7 Surrogate test samples 9 (Surrogate 2A and 2B), the materials are broken down by weight in grams.

Material	Substrate 1	Substrate 2	Substrate 3	Substrate 4	Copper Oxalate	Copper	Substrate 1	Substrate 2	Substrate 3	Substrate 4	Copper Oxalate	Copper
	Sample #2A						Sample #2B					
Hypalon- Neoprene	5.506						5.339					
Rubber glove with TBP	1.364	0.367			0.0112		2.1735	1.2082			0.0147	
Rubber glove with oil	1.4158	1.0995			0.0117		1.4681	0.9490			0.0114	
Metal tube with masking tape	32.4057	2.7770			0.0208		30.0829	2.9390			0.0225	
Weigh pan with stick & Vaseline & fitting	2.0373	1.4602	2.4070	89.3676	0.0333		1.9671	1.2331	2.7126	86.8609	0.0328	
PE bottle with PVC tape	10.3806	0.8935			0.0290		10.4189	1.0462			0.0249	
Nylon bag	6.6000					0.1060	6.5000					0.1063

Figure 2 Test sample #1 before use

3.4 TEST PROCEDURE

Each test was conducted as summarized below.

1. Fill the anolyte vessel with ~4.5 liters of 8M nitric acid, 0.5M silver nitrate
2. Fill the catholyte vessel with ~4.5 liters of 8M nitric acid
3. Switch on the hot plate (if needed) and allow the anolyte operating temperature to reach the pre-set value
4. Switch on the chiller
5. Ensure that chiller liquid is flowing through the condensers and the heat exchanger
6. Switch on the pumps and record the levels of the liquors by using the level indicators on the sides of the respective vessels
7. Add the 'waste sample' to the anolyte
8. Put the lid onto the anolyte
9. Take 20ml samples of anolyte and catholyte using the peristaltic pump. Label the samples. Record as time zero
10. Switch on the power supply and ultrasonic unit and set to the appropriate current and power ratings respectively
11. Record the current, voltage, anolyte temperature and record as time zero
12. Every two hours, take 20ml samples of anolyte and catholyte and record liquid levels, flow rate, current, voltage, anolyte temperature
13. End the experiment after the recordings have been made and the samples taken after the eighth hour
14. Switch off the power supply, ultrasonic source, hot plate, pumps
15. Upon completion of the experiment, analyze anolyte and catholyte samples as per the plan above (Cu^{2+} , Ag^+ , H^+ , TOC).
16. Carefully lift the basket from the anolyte vessel and allow to drain into the anolyte vessel for at least ten minutes
17. Place the basket into a plastic tray
18. Remove the treated samples and photograph
19. Weigh the treated samples
20. Analyze the samples for copper

3.5 ANALYTICAL PROCEDURES

The analytical procedures are included in Appendix 1. To summarize:

Analysis	Method
Silver	Potentiometric titration of a sample with potassium iodide until an excess of iodide is detected by a point of inflexion in the E vs volume characteristic. Based upon: $\text{Ag}^+_{(\text{aq})} + \text{I}^-_{(\text{aq})} \rightarrow \text{AgI}_{(\text{s})}$
Acid	Potentiometric titration of a sample with sodium hydroxide until an excess of base is detected by a point of inflexion in the pH vs volume characteristic. Based upon: $\text{H}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})}$
Copper in liquids	Atomic absorption using a Perkin Elmer 2380 spectrophotometer as per manufacturer's instructions
Copper in solids	Samples are placed onto a quartz tray and ashed at 800C for two hours. The samples are then digested twice (in the tray) using boiling aqua regia. The resulting slurry is filtered before liquid analysis of the copper
Total organic carbon	As per Hach method 10128 for high TOC. The results of TOC analyses were not found to be time dependent over the typical storage time of less than 2 days.

3.6 ANALYTICAL VALIDITY

The primary analysis is the determination of copper in the treated samples (Appendix 1). The validity of the proposed analytical method was determined as follows.

- ~0.115g of copper oxalate (from SRTC) were placed onto a polystyrene weigh pan.
- The weigh pan and copper oxalate were placed upon a quartz tray
- The quartz tray and samples were placed into the furnace and the temperature raised to 800C
- The temperature was maintained at 800C for two hours and then the oven was switched off
- The tray was removed from the furnace once the oven temperature had dropped below 150C
- The tray was allowed to cool to room temperature
- The remaining solids (barely visible) were digested twice in boiling aqua regia (3 parts concentrated HCl: 1 part concentrated HNO₃) as described in the method
- The solution was filtered and analyzed for copper by atomic absorption spectroscopy
- Three samples and three blanks were analyzed by this method. The results are provided in Table 8

Table 8 Analysis validity. Recovery of ~50mg copper from samples and blanks

Sample	Copper In Sample	Copper Recovered	% Recovery
Test 1	45.48mg	44.85mg	98.61%
Test 2	45.88mg	46.41mg	101.16%
Test 3	44.95mg	45.88mg	102.07%
Average = 100.61% Standard Deviation = 1.79%			
Sample	Copper In Sample	Copper Recovered	Maximum DF for 50mg Cu sample
Blank 1	0mg	0.18mg	277. 8
Blank 2	0mg	0.33mg	151.5
Blank 3	0mg	0.26mg	192.3
1. DF1 277.8, DF2 151.5, DF3 192.3, Mean maximum DF 207, Standard deviation on DF measurement = ± 64.5)			
2. Average copper recovered = 0.26mg, Standard Deviation on copper recovered = 0.08mg, Maximum DF from mean weight is 207 with a range of 325 and 153 (207 +118/-53).			

The results show a very small high bias to the recovery of the copper from the copper oxalate by using liquid analysis. The results in the remainder of the report have not been changed to account for this error. The blank result is only significant for samples containing

small amounts of copper. Arbitrarily, the blank discrepancy of 0.08mg has been included in calculations when the amount of copper present in the sample is less than 20 times this blank value (representing a 5 per cent error). Care should be taken in understanding the nature of the error in the DF calculation. The important data point is the 0.08mg variation in the measurement. This is reflected in the information that is presented in Table 9.

Table 9 Effect of 0.08mg error on calculation of DF as a function of weight of copper recovered from solids. Assumes a starting copper inventory of 50mg.

Weight recovered in mg	DF	DF low	DF high	DF variation	%Error in DF
0.26	192	278	147	192 (+85/-45)	+44%/-24%
0.5	100	119	86	100(+19/-14)	+19%/-14%
0.8	62.5	69	57	62.5(+6/-6)	+11%/-9%
1	50	54	46	50(+5/-4)	+9%/-7%
2	25	26	24	25(+1/-1)	±4%

Using this method of calculation, the maximum DF would be 192 (+85/-45). There would be a large error in the calculation of a DF of this value. For 1mg of copper recovered, the DF would be 50 (+5/-4). The potential error in the calculation of this DF value is very much lower than the potential error associated with the calculation of the DF of ~200.

3.7 CHEMICALS

Table 10 List of chemicals

Name	Purpose	Manufacturer	Grade
Nitric acid	Process chemical and analysis	Fisher Scientific	AnalaR
Silver nitrate	Process chemical and analysis	Fisher Scientific	AnalaR
Hydrochloric acid	Digestion chemical	Fisher Scientific	AnalaR
Sodium hydroxide	Analysis	Fisher Scientific	AnalaR
Potassium iodide	Analysis	Fisher Scientific	AnalaR
Deionized water	Preparation	Prepared using Elga Option 3 water purifier	$K \leq 1\mu S/cm$
Potassium hydrogen phthalate	Analysis	Fisher Scientific	AnalaR
Copper oxalate	Surrogate material	SRTC	As received
Copper nitrate	Analysis	Fisher Scientific	AnalaR

4 Result and discussion

4.1 DATA COLLECTED AND INTERPRETATION

4.1.1 Data collected

The process was designed to generate the data required to meet various requirements. How the data collected were used to meet these requirements is illustrated in Table 11.

Table 11 Meeting the objectives with the information collected during operation

Objectives	Parameters measured	Characteristics determined
The system shall produce no dioxins and furans	Not applicable	Historical evidence with SILVER II and other processes
The system shall be able to maintain near absolute containment of radionuclides	Descriptive	Plant description and experimental evidence
The system shall require minimal pre-treatment (sorting, size reduction, shredding) of the waste stream	Descriptive	The feed to the laboratory plant, used in the trials, is similar to the feed to the full-scale plant
The system shall produce waste forms that meet the Waste Isolation Pilot Plant Waste Acceptance Criteria	Copper concentration in liquids, waste volumes, copper in solids, dissolution of sample materials.	Surrogate DF > 100 (conservative limit) for the decontaminated solids. Organic dissolution characteristics. Metals dissolution characteristics. Potential for post-treatment handling.
The system shall produce waste forms that meet the TRUPACT-II packaging and shipping requirements	Copper concentration in liquids, waste volumes, copper in solids	Surrogate DF > 100 (conservative limit) for the decontaminated solids
The system shall demonstrate disposal paths for any secondary non-transuranic waste generated by the process	Descriptive	Disposal routes have already been demonstrated on inactive pilot-scale SILVERII plants
The system shall require minimal off gas control processes and monitoring instruments	Descriptive	Previous operating experience has demonstrated the simplicity, robustness and ease of control of the off-gas systems.
For decontamination systems - the system shall attain a minimal decontamination factor of 100	Copper concentration in liquids, waste volumes, copper in solids	Surrogate DF > 100 (conservative limit)
In addition, the data generated should enable scale-up estimates to be performed	Silver and acid in liquids, levels in plant, copper concentration in liquids, TOC in liquids	Rate of organic destruction, movement of chemicals and water within plant

The raw data from the ten tests are provided in Appendix 2. A complete set of the results is provided in graphical form in Appendix 4.

4.1.2 Data Interpretation Methods

Copper recovery versus time

We have already confirmed that copper present as copper oxalate on a plastic component can be recovered by:

- Ashing at 800C
- Digestion in aqua regia and filtration
- Analysis for copper in the filtrate using atomic absorption spectroscopy

The calculation used to determine the amount of copper present in the aqueous and solid phases is summarized below.

$$\text{Copper}_{\text{liquids}} = \text{Copper}_{\text{anolyte at time } t} + \text{Copper}_{\text{catholyte at time } t} + \sum_{\text{up to and including time } t} \text{Copper in liquid samples}$$

$$\text{Copper}_{\text{solids}} = \text{volume of digestion liquor} \times [\text{copper in digestion liquor}]$$

$$\text{Copper balance} = \frac{\text{Copper in solids at the start}}{\text{Copper in liquids and solids at the end}}$$

$$\text{DF} = \frac{\text{copper in solids at the start}}{\text{copper in solids post treatment}} \quad (\text{DF based upon solids})$$

Assuming mass balance :

$$\text{DF} = \frac{\text{copper in solids at the start}}{\text{copper in solids at the start} - \text{copper in liquids post treatment}} \quad (\text{DF based upon liquids})$$

Silver balance and transfer

The cell contains a porous ceramic membrane as a cell divider. Liquid can be transferred through this divider by imposing a differential pressure across the ceramic membrane. Liquids will flow slowly from the high pressure to the low-pressure side of the cell, and will carry the chemistry associated with that liquid transfer. Hence, should the anolyte move to the catholyte then both silver and dissolved copper will move from the anolyte to the catholyte.

We impose a potential across the membrane and pass a current through the cell. Current transfer is achieved by the movement of ions. Cations (silver (Ag^+) and protons (H_3O^+)) move towards the cathode and anions (NO_3^-) will move towards the anode. The ceramic membrane should not possess any permselectivity and hence the rate of transfer of the individual ions will depend upon their mobility and their concentrations.

Whichever transfer mechanism is involved, we should achieve a mass balance for silver in the system.

$$\begin{aligned} \text{Silver transfer from anolyte}_{\text{time}=t} &= \text{Silver transfer to the catholyte}_{\text{time}=t} \\ &= \text{Silver in anolyte and sample}_{\text{time}=0} - (\text{Silver in anolyte}_{\text{time}=t} + \sum_{\text{until time}=t} \text{Silver in samples}) \end{aligned}$$

A similar form of equation can be written for the catholyte silver.

Acid transfer

In the absence of direct reactions between organics and the nitric acid:

$$\begin{aligned} \text{Acid movement from anolyte} &= \text{Acid in anolyte and sample}_{\text{time}=0} \\ &\quad - (\text{Acid in anolyte}_{\text{time}=t} + \sum_{\text{until time}=t} \text{Acid in samples}) \end{aligned}$$

A similar calculation could be made for the catholyte except that acid will be lost during the run as NO_x produced by the reduction of nitric acid at the cathode.

Liquid transfer

As discussed above, liquids will flow slowly from the high pressure of the cell to the low-pressure side of the cell. The cell is operated with flow to the anolyte and catholyte compartments balanced so as to minimize the pressure differential (estimate to be < 5" WG) and hence liquid flow between the anolyte and catholyte solutions.

Liquid is also transferred with the moving ions. Current transfer is achieved by the movement of ions. Cations (silver (Ag⁺) and protons (H₃O⁺)) move towards the cathode and anions (NO₃⁻) will move towards the anode. Water will also move with these ions and the direction and amount of flow will depend upon the current, the amount of water associated with the ions and the number of the individual ions that are moving. For a non-permselective ceramic membrane, most of the current is passed by the proton (H₃O⁺). This ion also carries more water than the other ions present in the system (Ag⁺ and NO₃⁻). Hence, we would expect some water transfer from the anolyte to the catholyte that is associated with ion transport.

$$\begin{aligned} \text{Liquid movement from anolyte} &= \text{Liquid in anolyte and sample}_{\text{time}=0} \\ &\quad - (\text{Liquid in anolyte}_{\text{time}=t} + \sum_{\text{until time}=t} \text{Volume in samples}) \end{aligned}$$

However, current that is not used in oxidizing organics will be used to oxidize water in the anolyte:

Nitric acid reduction at the cathode to nitrous acid, involves the generation of water:

We would therefore expect a water loss from the anolyte associated with oxidation and a water gain in the catholyte associated with nitrate reduction. The stated case is an oversimplification:

- Water is produced in the anolyte by organic oxidation
- Water can be both gained and lost from the catholyte by complex gas formation and reformation reactions

Quantification of the anolyte reactions is simpler than the catholyte reactions since the former can be estimated by understanding weight changes in the organic samples, whereas the latter requires gas analysis to be performed. This is outside the scope of this preliminary study.

4.2 DATA SUMMARY (TESTS 1-7)

A summary of the interpreted data is provided in Table 12.

Table 12 Summary of the copper recovery data (tests 1-10)

Test	T/ C	US/ W	Cu in sample/m g	Recovery details %	Start organic (grams)	Change in Organic (grams)	Duration for colorless anolyte solution
1	60	0	205.29	57.70 in anolyte, 8.80 in catholyte, 15.51 in solids 82.02 total (DF 6.45)	51.00	20.44	2-3 hours
2	60	100	200.74	51.76 in anolyte, 7.88 in catholyte, 16.14 in solids 75.78 total (DF 6.20)	50.03	19.13	2-3 hours
3	80	200	194.65	62.90 in anolyte, 8.22 in catholyte, 6.47 in solids 77.59 total (DF 15.45)	48.56	23.35	5 hours
4	45	100	196.35	59.26 in anolyte, 13.17 in catholyte, 27.25 in solids 99.68 total (DF 3.67)	49.42	15.62	2-3 hours
5	80	0	201.09	66.80 in anolyte, 3.43 in catholyte, 26.60 in solids 96.83 total (DF 3.76)	48.45	17.56	4-5 hours
6	60	150	198.92	66.75 in anolyte, 4.12 in catholyte, 26.90 in solids 97.77 total (DF 3.72)	50.07	13.42	2-3 hours
7	60	150S	203.11	69.01 in anolyte, 5.96 in catholyte, 17.25 in solids 92.22 total (DF 5.80)	50.02	15.20	2-3 hours
8	60	150S	51.53	57.54 in anolyte, 7.30 in catholyte, 13.58 in solids 78.43 total (DF 7.36)	47.86	13.22	3-4 hours
9	60	150S	53.38	93.56 in anolyte, 4.96 in catholyte, 1.57 in solids 100.09 total (DF 63.74)	36.41	12.54	3-4 hours
10	60	150S	54.18	74.23 in anolyte, 4.17 in catholyte, 5.43 in solids 83.83 total (DF 18.43)	46.60	19.10	3-4 hours

4.3 PROCESS OPTIMIZATION

Tests 1-7 were used to optimize the combined SILVER II/ultrasonic process. The objectives being to maximize both copper decontamination as well as partial mineralization of the organic content of the surrogate waste. The copper in the system was monitored by determining both the copper content of the electrolytes (anolyte and catholyte) as a function of time as well as the copper in the remaining solids at the end of the run. The results are summarized in Table 12, and graphically in Figure 3 to Figure 5. In examining these figures it is evident that:

- The rate of copper release is only slightly affected by changing the operating temperature and the power and mode of the ultrasonic agitation
- High temperature (80C) increases the rate of organic attack
- The combination of high temperature (80C) and high ultrasonic power (200W) significantly enhances the rate of organic destruction
- A swept mode ultrasonic method is more effective than the static mode of operation

Figure 3 Variation of recovery of copper (in solution) as a function of time

Figure 4 Variation of final amount of copper dissolved from substrates as a function of temperature and ultrasonic power - radius is proportional to the recovered copper as a percentage

Figure 5 Variation of amount of organic material lost from substrates as a function of temperature and ultrasonic power - radius is proportional to the weight change

The observations from the photographs in Figure 12 to Figure 17 (Appendix 3) and the weight changes are combined in Table 13. The nylon bag and the paper towel were destroyed under all conditions. The handiwipe (mainly finely woven polypropylene) was badly damaged in all of the tests and the contents of the polythene bag were attacked, although solution access was not totally successful. The PE and RTV were not substantially attacked, the epoxy and PS were discolored and epoxy was embrittled to the extent there was partial break-up of this substrate in some of the tests. It is uncertain whether all of the epoxy was recovered from the sample basket at the end of the run.

Table 13 Weight changes and observations of substrate damage during tests 1 to 7

Test	US /W	T /C	D weight /g	Organic destroyed /g	Materials badly damaged or missing	Materials not affected
1	0	60	20.44	13.8	Paper, nylon bag, most of handiwipe, epoxy dislodged, PE bag contents partially	PE, PS (only slightly), RTV, some of the epoxy as discolored lump
2	100	60	19.13	13.8	Paper, nylon bag, most of Handiwipe, epoxy dislodged, PE bag contents partially	PE, PS (only slightly), RTV, some of the epoxy as discolored lump
3	200	80	23.35	28	Paper, nylon bag, most of Handiwipe, epoxy dislodged, rubber, PE bag contents partially	PE, PS (only slightly), RTV, some of the epoxy as discolored lump
4	100	45	15.62	13.8	Paper, nylon bag, most of Handiwipe, epoxy dislodged, PE bag contents partially	PE, PS (only slightly), RTV, some of the epoxy as discolored lump
5	0	80	17.56	20	Paper, nylon bag, most of Handiwipe, rubber dislodged, PE bag contents partially	PE, PS (only slightly), RTV, some of the epoxy as discolored lump
6	150Sw	60	13.42	13.8	Paper, nylon bag, most of Handiwipe, epoxy dislodged, PE bag contents partially	PE, PS (only slightly), RTV, some of the epoxy as discolored lump
7	150Sw	60	15.2	13.8	Paper, nylon bag, most of Handiwipe, epoxy dislodged, PE bag contents partially	PE, PS (only slightly), RTV, some of the epoxy as discolored lump
Sw = frequency sweep						

The combination of organic attrition and reactive inorganic dissolution (copper oxalate) results in the surrogate decontamination of the wastes. In section 3.6, it was possible to achieve quantitative recovery of copper from a copper oxalate contaminated organic substrate. Hence:

$$\text{Cu}_{(\text{sample, time}=0)} = \text{Cu}_{(\text{electrolyte, time}=\text{end})} + \text{Cu}_{(\text{samples, time}=\text{end})}$$

The copper balances are presented in percentile terms in Table 12, and displayed graphically in Figure 6.

Figure 6 Variation of copper recovered (electrolyte, solids, total) as a function of test number

It is evident from the figure that the copper recovery into solution was achieved by using a combination of the electrochemistry and ultrasonics, with test 7 providing the best results.

As expected, the total recoveries during tests 1-3 were poor (~80%) as opposed to ~97% for tests 4-7. Copper cannot be lost from the system. On the basis of the poor early results, significant care was taken in the later experiments to recover even small pieces of the waste. The DF values calculated in Table 12 refer to the copper found in the solids. This value may be optimistic, since we have been unable to account for up to 25% of the copper (test 2). In Figure 7, the DFs as calculated from both the solids and the electrolyte are provided. The maximum DF for the solids was for test 3 (80C/200W). It is important to note that the only solid with visible copper present was the RTV sample (~10% of the total copper) (see Figure 8) and hence the expected DF would be ~10 (c.f. calculated result of 15.45). Failure to mineralize both the RTV and epoxy would yield a maximum DF of 6, and only 3.4 if the contents of the polythene bag are added to the copper contribution.

The DF based upon electrolyte contents appears to offer the more accurate decontamination factor based upon purely visual observations, this is related to being unable to quantitatively recover finely broken up solids from the system. Such a statement would not be true in the event of a high degree of substrate decontamination and subsequent capture for ashing and digestion. In section 3.6, a maximum solids DF of ~207 was demonstrated. In the same section, the standard deviation for three electrolyte analyses of ~1.7% for quantitative copper recovery to solution would limit the maximum DF measurable to approximately 30 by errors in the electrolyte analysis. Hence, for $DF < 30$, solution analysis is the most appropriate option, solids analysis should be used in calculations for $DF \geq 30$.

Figure 7 Variation of DF based upon solids content and electrolyte content as a function of test number

Figure 8 Copper distribution with components of sample 1 (other samples very similar)

The objective is to provide a process that can both destroy reactive organic components, such as cellulose based materials, as well as decontaminate the surfaces of unreactive components (such as PVC and PE). Complete organic destruction is not desirable since this will increase the plant size. The conditions that fulfill this objective are:

- Run at 60C
- Operate with 150W swept ultrasonics
- Expect RTV and epoxy to be recalcitrant
- Expect performance to be poor if the solution cannot access the contaminated surface

4.4 SURROGATE TEST 8-10

4.4.1 Data Summary

Surrogate tests were performed following the optimization trials. This section reviews these tests against the performance criteria. The tests were conducted as per Table 14 with the results summarized in Table 15. Test 8a was an agreed extension of test 8. The solids results for post-treatment surrogate 1A are only available at the end of test 8a. No liquid samples were collected during test 8a. The duration for the colorless anolyte solution refers to the time taken (from the start of the test) for the anolyte solution color to become brown/black, i.e. rich in Ag(II). Figure 9 and Figure 10 illustrate the distribution of the copper on these samples.

Table 14 Operating conditions for tests 8 to 10

Test Number	Conditions
Test 8	60C, 150W swept, 8 hours surrogate 1A
Test 8a	60C, 150W swept, 8 hours surrogate 1A continued
Test 9	60C, 150W swept, 8 hours surrogate 2A
Test 10	60C, 150W swept, 8 hours surrogate 1B with some of the samples cut to 1/2 inch pieces (tubing, PS weighing boat, PE bottle), titanium mesh inserted to ensure that the samples were kept submerged

Table 15 Summary of the copper recovery data (tests 8-10)

Test	Recovery details %				D Organics g	Silver transfer	Liquid transfer liters	Acid balance	Duration for colorless anolyte solution
	Anol.	Cath.	Solids	DF (sol/liq)					
8	57.54	7.30		()/2.8	13.22	~0.5 moles A-C in 8 hours	~0.8 anol loss ~0.4 cath gain in 8 hours	~7 moles lost	3-4 hours
8a			13.58	7.4/()					
9	93.56	4.96	1.57	63.7/67.6	12.54	~0.3 moles A-C in 8 hours	~0.22 anol loss ~0.37 cath gain in 8 hours	~3 moles lost	3-4 hours
10	74.23	4.17	5.43	18.4/4.6	19.10	~0.3 moles A-C in 8 hours	~0.2 anol loss ~0.05 cath gain in 8 hours	~7 moles lost	3-4 hours

Figure 9 Starting copper distribution on samples surrogate #1A for experiment 8 (remaining materials were not contaminated with copper oxalate)

Figure 10 Starting copper distribution on samples surrogate #2A for experiment 9 (remaining materials were not contaminated with copper oxalate)

4.4.2 Achieve the recovery of surrogate copper from the samples (DF ³100)

The surrogate samples (as detailed in Table 6 and Table 7) were all contained within a sealed nylon bag. This bag was destroyed during every test. The major differences between these surrogate samples and those tested during optimization were:

- There was no RTV in any sample
- Samples 1-7 and Surrogate 1A and 1B contained copper oxalate loaded epoxy
- Surrogate 2A and 2B did not contain epoxy
- Surrogate 1A and 1B contained copper oxalate within a Tygon pipe bounded by two corks

The results are summarized in Table 15.

4.4.2.1 Test 8

In test 8, approximately 64% of the copper were found in the solution at the end of the eight-hour period. A visual examination indicated that:

- The oil dry was missing (vermiculite type materials tend to delaminate and be dispersed by the acid conditions used in SILVER II).
- The paper towel, wooden stick, nylon bag, one of the corks, and pump oil deposits had all been mineralized
- The HEPA filter, the other cork, handiwipe had all been badly attacked
- The epoxy in the bottle was badly discolored but still appeared to be in one piece
- The Tygon tubing was discolored and warped and there was blue copper oxalate on one of the surfaces in the middle of the tube
- The PVC components were crinkled and any glue had been largely removed from the surfaces
- The PS weigh pan was discolored
- The PE bag seemed to have been unaffected, although the contents had been attacked but had not been destroyed
- The PE bottle seemed to have been unaffected
- The PVC coating had been removed from the glass slide
- The vial had been decontaminated
- There was visible evidence of the blue copper oxalate in the middle of the Tygon tube, and possibly very small amounts in the PE bag

After a discussion with the SRTC customer, it was agreed that access to the center of the Tygon tube and to the inside of the PE bottle and bag was restricted. A decision was made to increase the run duration. The samples were returned to the anolyte vessel and the run continued for another eight hours. At the end of this period, from visual examination, most of the copper was removed from the tubing and the second cork had been destroyed (although a small amount of copper oxalate was visible in the middle of the tube). The weight of copper in the tube at the start of the run was 9.18mg. By the end of the extended run, only 1.28mg remained, an 86% removal. It is important to comment that 1.28mg of

copper (as oxalate) was readily visible to human eye. A visual examination is a good starting point for an assessment of the degree of decontamination for this surrogate. A substantial amount of the epoxy was present as red/brown shards. The PS weigh boat had been reduced to small pieces. By the end of the extended run, only 14% of the copper could be found on the remaining samples. From visual observations, most of the residual copper was present in the epoxy with traces in the Tygon tube and possibly some in the polythene bag. This test demonstrated that solution access to the contaminated site is very important and that the rate of attack on the epoxy is slow under these conditions.

4.4.2.2 Test 9

In test 9, approximately 98.5% of the copper were found in the solution at the end of the eight-hour period. A visual examination of the decontaminated surrogate waste indicated that:

- The Hypalon side of the rubber composite was badly discolored and blistered
- The Neoprene side of the rubber composite was discolored and friable
- Rubber glove with TBP had been destroyed
- Rubber glove with oil had been destroyed
- The masking tape was damaged and detached from the metal tube, the tube had been etched
- The weigh pan had been discolored, embrittled, and the edges attacked. The stick and Vaseline were destroyed and the metal fitting had been etched
- The PVC tape surrounding the PE bottle had been attacked; the PE bottle had not been noticeably attacked
- The nylon bag had been destroyed
- There was no visible evidence of the blue copper oxalate

The samples were ashed, digested and filtered, and the copper content in the filtrate was found to be ~0.8mg (1.5%), corresponding to a surrogate DF of 64.

4.4.2.3 Test 10

In test 8, it was demonstrated that effective solution contact is an important prerequisite for decontamination. In the full scale system it is envisaged that the samples will be size-reduced to approximately ½". It is also important to ensure that the samples are submerged in the anolyte vessel. The samples from surrogate #1B (essentially the same as #1A) were size reduced as follows.

- The Tygon tube was chopped into ½" pieces and the corks left in the end pieces
- The PE bottle and PS weigh boat were both chopped in half

The samples were placed into the anolyte vessel and circle of titanium mesh was used to ensure that the samples were submerged. Approximately 78% of the copper were found in the solution at the end of the eight-hour period. A visual examination of the samples indicated that:

- The oil dry was missing
- The paper towel, wooden stick, nylon bag, both of the corks, and the pump oil deposits had all been mineralized

- The HEPA filter and the Handiwipe had all been so badly attacked that it was not possible to identify the individual components
- The epoxy in the bottle-halves was missing, but there were shards of red material that were assumed to be denatured epoxy
- The Tygon tubing was discolored and warped and there was no blue copper oxalate in any of the pieces
- The PVC components were crinkled and any glue had been removed from the surfaces
- The PS weigh pan was discolored and the edges had been attacked
- The PE bag seemed to have been unaffected, although the contents had been destroyed
- The PE bottle itself seemed to have been unaffected
- The PVC coating had been removed from the glass slide
- The vial had been decontaminated
- There was no visible evidence of the blue copper oxalate but the fibrous samples (possibly the remains of the HEPA filter and Handiwipe) seemed to contain a significant amount of red discoloration, possibly remains of the copper-loaded epoxy

The samples were ashed, digested and filtered, and the copper content in the filtrate was found to be nearly 3mg, corresponding to a surrogate DF of 18 (~95%). This is much larger than 78% of the copper found in the solutions. The conclusion is that many of the degraded epoxy shards were still in the rig. The actions of sample size reduction and submerging the samples has substantially improved the performance of the unit. Even so, the system does not destroy epoxy under the conditions studied. This is of little consequence since samples of loaded epoxy will not be present in the real waste.

4.4.3 Achieve mineralization of the reactive samples

There are three indicators that can be used to estimate the rate of mineralization of organic samples.

Parameter

Critique

The weight change in a given time.

It is very difficult to rinse thoroughly acid and silver from small porous and fibrous test samples and then to dry such samples without affecting those materials. The samples were drained and allowed to dry in air before ashing. Weight change results should be regarded as approximations.

The time required for the anolyte to go brown-black

The time for the anolyte to go brown-black (indicative of an excess of the Ag(II) nitrate complex) ultimately depends upon the rate of removal of the complex by reactions with organic species (in solid, liquid and dissolved forms) and water. Organic substrates that react directly with the nitric acid will produce nitrous acid that rapidly reacts with the Ag(II). Organic substrates may be reacting (slowly) even when the solution has darkened.

Parameter**Critique**

The colour can be used as an indicator that only the reactive organics have been destroyed.

Changes in solution TOC

The anolyte TOC will rise during the treatment of wastes containing readily oxidized materials (such as cellulose). The TOC rises rapidly since the products of the reactions with both Ag(II) and nitric acid are more soluble in the anolyte than the parent material. The solubilized species are often more reactive than the solid wastes because the reactions become homogeneous as opposed to heterogeneous and, hence, are not affected by surface area effects. For a batch process, the TOC should rise and then fall as the readily attacked species are solubilized and destroyed. The peak TOC and the rate of decrease should provide an indication of the rate of organic destruction. The rate will be affected by surface area of the solid wastes, temperature, mixing (ultrasonic power) and the availability of the reactive surfaces.

Table 16 Components in surrogate wastes (1A) with totals for 'reactive' materials. All weights in grams (substrate refers to the individual components, e.g. Tygon, 2 corks, TBP is three substrates).

Material	Substrate 1	Substrate 2	Substrate 3	Substrate 4
Surrogate material #1A (1B similar)				
HEPA filters	1.0282			
Tygon with 2 corks and TBP	9.6229	0.4746	0.7876	
Weigh pan	1.9528			
Handiwipe	1.9335			
Paper towel	2.4294			
PE bottle with epoxy and stick	6.3074	2.9195	1.3021	
Nylon bag	6.3			
Glass with PVC coating	5.5759	0.5472		
Oil dry	3.3674			
Vial with pump oil*	12.1435	0.5069		
Atomic swipe	3.773			
PE bag with PVC tape and pump oil	2.1856	1.4991	0.8134	
Total/g	18.3205	D_{organics} = 13.22g (8), 19.10g (10) D_{organics} = 72% (8), 104% (10)		

Table 17 Components in surrogate wastes (2A) with totals for 'reactive' materials. All weights in grams (substrate refers to the individual components, e.g. Tygon, 2 corks, TBP is three substrates).

Surrogate material #2A (2B similar)				
Hypalon-Neoprene	5.506			
Rubber glove with TBP	1.364	0.367		
Rubber glove with oil	1.4158	1.0995		
Metal tube with masking tape	32.4057	2.777		
Weigh pan with stick & Vaseline & fitting	2.0373	1.4602	2.407	89.3676
PE bottle with PVC tape	10.3806	0.8935		
Nylon bag	6.6			
Total/g	14.7135	D_{organics} = 12.54g (9)		
		D_{organics} = 85% (9)		

The weights of the individual components and the totals for the "reactive" components are provided in Table 16 and Table 17. The changes in weight during the treatments have also been included. The reactive components were selected from experimental evidence; i.e. those materials that were either destroyed or were very badly damaged by the treatment process. Examination of the data confirms that ensuring contact of the reactive medium with the organic wastes results in reactive organic mineralization (c.f. tests 8 (72%) and 10 (104%)).

A judgment also needs to be made as to how rapidly these materials were destroyed. In Table 15, the time taken for the anolyte to go brown-black was between three and four hours in all three surrogate tests. The conclusion is that the bulk of these materials were destroyed in the first four hours. The conclusion is further validated by examining the TOC data (Figure 11). The TOC data indicates that:

- The rate of destruction of solubilized TOC is proportional to the amount present (linear log response).
- The rate of organic solubilization, as evidenced by the anolyte TOC, dropped to a very low value within the three to four hour period.

A low TOC value would also arise if the rate of mineralization (soluble TOC to CO₂) were extremely fast. Such a rapid reaction would be accompanied by solution decolorization, and so the former conclusion would seem to offer the most valid explanation for the observations and data.

Figure 11 Variation of the TOC (in grams total) with time and normalized TOC (in grams total) with reference to the maximum TOC value. Surrogate tests 8 and 9. Shaded bars reflect limits for semiquantitative accuracy in analysis.

4.4.4 Provide data that enables scale-up estimates to be made

The following information is needed to assist with the scale-up of this process from laboratory to pilot scale.

4.4.4.1 Rate of decontamination

The rate of copper release to the solution system is the primary measure of the rate of decontamination. In Figure 88 (Test 8) and Figure 97 (Test 9) the time required to reach a constant amount of copper was four and eight hours respectively. It was also during Test 9 that the highest DF was achieved (~64). It is appropriate to take this value as our processing rate for this surrogate waste. Thus a 60A electrochemical cell operating in tandem with a 150W swept ultrasonic anolyte vessel was able to decontaminate 158g of waste within an eight hour period (~20g per hour).

4.4.4.2 Rate of organic destruction

The rate of organic destruction was estimated from weight change, color change and TOC data. In test 10 we were able to destroy ~19g in the eight-hour period. Most of the material was destroyed in the first four hours. Hence, for a mixed cellulosic/nylon waste, the rate of destruction was approximately 4.8g per hour. These experiments treated batches of waste. Continuous operation would be more effective than batch since the 'organic loading' within the system can be maintained and hence the rate of organic destruction maximized. From the TOC data (Figure 11), we can estimate that the rate of mineralization of the solubilized components in the first two hours was approximately 1.7 times faster than over the first four hours. Thus the maximum rate of cellulosic/nylon destruction (for this weight and type of waste) can be estimated to be ~8g per hour.

The maximum rate of organic destruction as a proportion of the current can be calculated from the knowledge of the molecular formula of the organic material and by assuming that the each elemental component is oxidized to its highest stable oxidation state:

- C to CO_2
- N to NO_3^- (HNO_3)
- to O_2
- H to H^+
- P to PO_4^{3-} (H_3PO_4)

Calculation of the molecular formula ($\text{C}_{0.92}\text{H}_{1.7}\text{N}_{0.056}\text{O}_{0.294}\text{P}_{0.003}$) (and approximations) are included in Table 18. From the formula, we can calculate that the treatment rate would be 8.08g per hour for a 60A unit. This corresponds to the maximum rate estimated above for a continuous process. The maximum current efficiency (as estimated from test 10) was 100%. The same parameter can also be calculated for test 9 during which the maximum destruction rate was 6.27g per hour of a mixture of rubber, nylon and oil also corresponds to a current efficiency of 100%. The efficiency in test 8 was 70%, and this difference (test 8 to 10) reflects contact issues that were addressed by the changes made to the anolyte vessel before test 10.

Table 18 Approximate molecular formula for mixed 'reactive' organic materials (sample #2A)

Material	Weight /g	C	H	N	O	P	Moles C	Moles H	Moles N	Moles O	Moles P
Cellulose (corks, towel, stick, swipe)	7.9791	7	12	0	5	0	0.317	0.544	0	0.227	0
Nylon (nylon bag)	6.3	12	22	2	2	0	0.335	0.613	0.056	0.056	0
Oil (oil and Handiwipe (polypropylene))	3.2538	12	24	0	0	0	0.232	0.465	0	0	0
TBP (TBP)	0.7876	12	27	0	4	1	0.036	0.080	0	0.012	0.0030
Molecular formula							0.920	1.702	0.056	0.294	0.003

To conclude, highly reactive materials can be treated with unity current efficiency so long as good contact is achieved between the substrate and the anolyte. The current efficiency for the less reactive materials is difficult to estimate, but is likely to be less than 10%. It is important to stress that a high current efficiency is not desirable for the 'unreactive' materials, since the priority is to decontaminate such substrates by surface attack as opposed to using current in their destruction.

It is also important to observe that the results indicate that it is the decontamination (copper release in this case) and not the cellulosic organic destruction that is the rate limiting step in this process. The reactive organics were largely destroyed in the first four hours, as opposed to requiring eight hours of treatment for the near quantitative recovery of the copper from the surrogate wastes.

4.4.4.3 Rate of and direction of chemical transfers

A summary of the changes in the chemical and liquid contents of the anolyte and catholyte vessels are provided in Table 19. The cell contains two ceramic membranes as separators. These are solution permeable, and the flow rates to the cell were controlled with the objective of minimizing hydraulic transfers based upon pressure differentials across these porous materials.

Table 19 Chemical changes during test 8-10 (eight hours)

Test	Silver transfer moles	Liquid transfer liters	Acid balance moles
8	~0.5 Anol to Cath	~0.8 anol loss ~0.4 cath gain	~7 lost (-8C, 1A)
9	~0.3 Anol to Cath	~0.22 anol loss ~0.37 cath gain	~3 lost (-8.5C, +3.5A)
10	~0.3 Anol to Cath	~0.2 anol loss ~0.05 cath gain	~7 lost (-11C, +4A)

Liquid

For a 60A cell, we would expect to lose a maximum of 160mls of water in eight hours from the anolyte by oxidation to oxygen. The amount of water generated by oxidation of the organics is very small and has been ignored. The rate of gain of water in the catholyte by reduction of nitric acid depends upon the product of the reduction.

The maximum rate of water production at the cathode would be for NO₂ release. For a 60A cell, we could generate as much 320mls of water in eight hours. Hence, we might expect up to 160mls of loss from the anolyte and 320mls of gain to the catholyte based solely upon electrochemical reactions at the anode and cathode. Some of the anode current is consumed in organic oxidation, but at most this is ~25% over the full eight hours of the run, and so the anolyte loss figure should be altered to 120mls in eight hours. This is before any losses associated with pressure differences or electro-osmotic effects. We have deliberately ignored evaporative losses because of the presence of the condensers.

Given these losses and gains, we do not achieve water balance during these tests. At most we are losing 0.4 liters of liquor during the test (~4%). We did experience problems with the anolyte level gauge from test 8 onwards because of a blockage caused by the oil dry material and so the measurements need to be regarded as estimates. For an organic membrane, such as Nafion, we would expect to transfer around 270ml of water from the anolyte to the catholyte in 8 hours at 60A. Such an amount would be lost in the errors experienced in measuring liquid levels in these tests. It is difficult to compare systems since the reading errors were significant.

To summarize, the liquid transfer rate that was measured was small and could be controlled by appropriate pressure control within the cell.

Silver

The 0.3 moles transferred during tests 9 and 10 would require 0.6 liters of anolyte to be hydraulically transferred. Such a transfer was not evident in either test. If we assume that there was no bulk hydraulic movement, then we are electrolytically transferring approximately 0.3 moles of silver from the anolyte to the catholyte during the eight-hour tests. This corresponds to 1.6% of the current used for silver transfer. Calculations using simple ionic mobility and ionic concentrations of 0.5M Ag⁺, 8M H⁺ and 8M NO₃⁻ would predict a transfer rate corresponding to 0.9% current efficiency for the silver assuming no permselectivity for the ceramic membrane.

To summarize, we will assume that:

- There is a transfer of silver from anolyte to catholyte and that the rate of transfer corresponds to 1.6% of the measured current

Acid

In the absence of bulk hydraulic transfers, the movement of nitrate in the unit will depend upon the form of losses from the cathode and ionic movement from catholyte to anolyte through the ceramic membrane. In the absence of permselectivity, we would expect to:

- Transfer 0.37 moles per hour of nitrate from the catholyte to the anolyte (this corresponds to 3 moles in an eight-hour run)
- Lose 2.2 moles per hour if the product is NO_2 (this corresponds to -17.6 moles in an eight-hour run)

On average (tests 8 to 10) only 9 moles of acid were lost from the catholyte and 2.8 moles gained in the anolyte. The implication of the former is that the cathode reaction is producing primarily NO that will react with oxygen in the air to produce NO_2 .

The information presented in the table indicates a significant spread in the loss/gain data.

To summarize:

- The transfer of nitrate from catholyte to anolyte is controlled by ionic mobility with a non-permselective membrane
- The rate of loss of acid in the gas phase from the catholyte is based upon the reduction of nitric acid to nitric oxide

5 Conclusions

The conclusions will be framed around the program objectives as laid out in Table 11.

Objective 1 - The system shall produce no dioxins and furans

'Dioxin' is a collective term for the family of compounds known as polychlorinated dibenzodioxins (PCDD). Similarly, furan refers to the family of compounds known as polychlorinated dibenzofurans (PCDF). There are 210 compounds within these two families. Generally, compounds with chlorine present at the 2,3,7,8 positions within the molecules have the greatest potential toxicity. Hence, levels of dioxins and furans are typically reported in terms of a toxic equivalent (I-TEQ) to 2,3,7,8 dibenzo-dioxin using an international scale of toxicity for each congener.

The groups of compounds originate from high temperature processes. Processes that have been shown to have the potential for dioxin and furan emissions include solids waste incineration, sinter plants and electric arc furnaces. Two main mechanisms have been proposed to describe the formation of PCDD/PCDF during combustion processes.

- De novo synthesis
- Precursor route

A combination of the two mechanisms may occur.

De-novo synthesis

De-novo synthesis is considered one of the major mechanisms for PCDD/F formation in high temperature processes. The PCDD/Fs are formed by heterogeneous reactions of gaseous chlorine and aromatic compounds on particles of dust that are in the off-gas stream. The reaction is believed to be catalyzed by metal species that form metal chlorides on the surface of the dust particles. These intermediates then react with the aromatic compounds. There is a specific temperature window for the formation of these species, and the PCDD/Fs are actually formed when the flue gas is cooled to this temperature window of 250-450C.

Precursor route

The precursor route also involves the metal-catalyzed reaction of species on dust particles in the temperature range of 250-450C. In this mechanism, aromatic species related to PCDD/Fs react on the surface of the dust particles in the presence of a catalyst.

For either of the above mechanism to occur, the following must be available:

- Solid particles containing carbon structures
- Organic or inorganic chlorine
- Copper or iron ions (possibly zinc or manganese)
- An oxidizing atmosphere
- A temperature window of 250-450C

Table 20 shows that many of these conditions are not applicable to the SILVER II process. During previous SILVERII work⁴ at a 2kW scale dioxin and furan analyses were performed for liquid and solids streams. The PCDD concentrations found in the samples were also found in the process blanks at the 11 pg/liter for OCDD.

Table 20 Applicability of PCDD/F formation conditions to SILVER II

Conditions required for PCDD/F formation	Applicability to SILVER II
Solid particles containing carbon structures	Wet environment suppresses dusts
Organic or inorganic chlorine	Potentially present at low concentrations
Copper or iron ions (possibly zinc or manganese)	Potentially present if metals added to the process
An oxidizing atmosphere	Present
A temperature window of 250-450C	Not present (Maximum temperature <100C)

The process does not produce PCDD/Fs and the conditions leading to PCDD/F production are not present within SILVER II.

Objective 2 - The system shall be able to maintain near absolute containment of radionuclides

Gas phase vapor releases are eliminated by using condensers on both the anolyte and catholyte off-gases.

The system is able to maintain near absolute containment of radionuclides.

Objective 3 - The system shall require minimal pre-treatment (sorting, size reduction, shredding) of the waste stream

As with all methods that utilize reactive liquids to treat solids wastes, the process efficacy is maximized by ensuring that the solution contacts the contaminated surfaces. A standard shredding process has been proposed for full-scale implementation and the significance of size reduction was demonstrated during test 10.

Sorting will not be necessary since the process has successfully:

- Destroyed cellulosic materials, simple rubbers, and organic liquids
- Decontaminated materials that will be present in the real wastes

⁴ Demonstration II Final Report for PMACWA– May 2001–by AEAT/CH2MHill

Objective 4 - The system shall produce waste forms that meet the Waste Isolation Pilot Plant Waste Acceptance Criteria (WIPP WACC)

The WIPP WACC are organized under five major headings: Container Properties, Radiological Properties, Physical Properties, Chemical Properties, and Data Package Contents. As regards this specific program, the major acceptance criteria for WIPP acceptance are associated with achieving a low hydrogen production rate by reducing the radionuclide inventory. A conservative Pu DF target of 100 has been set to meet this criterion, although we have been advised by SRTC that a DF of >60 would be needed to meet the hydrogen generation criterion. We have demonstrated a surrogate DF of 64 for copper oxalate. Duplication of this DF with real Pu contaminated material would meet this WIPP waste acceptance criteria.

We have also demonstrated that we can reduce organic content of the wastes by efficiently mineralizing components such as cellulose, simple rubbers and oils.

Objective 5 - The system shall produce waste forms that meet the TRUPACT-II packaging and shipping requirements

We have demonstrated a surrogate DF of 64 for copper oxalate. Duplication of this DF with real Pu contaminated material would meet packaging and shipping requirements.

The final process will need to eliminate nitric acid from the remaining solid waste. This was demonstrated during the ACWA programme⁴, during which we produced over 500kg of a solid silver chloride material that was easily rinsed to produce a near-neutral filtrate ($\text{pH} > 4$). This material was transported to an off-site silver recovery plant in standard DOT compliant containers.

In addition to this task, several samples of solids were cleaned by simple rinsing to pH4 by using 50-liter filter bags.

In full-scale designs, all rinse water is recycled back to the plant.

Objective 6 - The system shall demonstrate disposal paths for any secondary non-transuranic waste generated by the process

The laboratory process vented oxygen, carbon dioxide, carbon monoxide, and NO_x. There was no other secondary non-transuranic waste produced since the anolyte and catholyte would contain all the Pu dissolved from the solid materials.

In the event that direct venting is deemed inappropriate, then the NO_x can be removed by using a caustic peroxide scrubber. The use of such NO_x scrubbers is commonplace within the DOE Complex and no further description is necessary. Consideration to materials that will be solubilized by the SILVER II process is given in Table 21.

Table 21 Non-transuranic waste produced in liquid phase

Waste form	Fate
Acids and bases may exist either as dried residue or as liquid trapped in containers – hydrochloric acid, nitric acid, sulfuric acid, and caustic soda	The hydrochloric acid is converted to solid silver chloride that will stay with the solid phase. Sulfuric acid will stay in solution. Should the concentration rise to greater than 0.5 mole litre ⁻¹ then this will need to be removed by distillation. Such a process was demonstrated as part of the ACWA program. Excess nitric acid can also be recovered in the distillation process
Chlorinated hydrocarbon solvents would not be expected to be above the parts per million range in the air space, however, they could be present in the liquid form trapped in containers (bottles, cans) – carbon tetrachloride, chloroform, perchloroethylene, trichloroethylene, etc.	Chloro-organics are converted to carbon dioxide, water, and silver chloride. The solid will remain with the solid phase
Combustibles may exist as liquids trapped in containers - acetone, isopropyl alcohol, and methanol	These materials are mineralized to carbon dioxide and water
Radionuclides of concern in the actual wastes include primarily sub-micron ²³⁸ PuO ₂ particles. Trace amounts of other transuranics may also be present (plutonium-239, plutonium-241, etc.)	All plutonium is dissolved and is found in the form of Pu(VI)
Toxic metals would be present in the solid form such as cadmium coated materials, chromium coated materials, lead coated materials, leaded gloves (lead shot in rubber gloves), mercury coated materials, and mercury thermometers	The metals are dissolved in SILVERII. Lead can be oxidized to lead dioxide on the anode. This can be removed readily by rinsing with a simple organic acid (such as formic acid). Ultimately, metal concentrations of <0.25 mole litre ⁻¹ can be tolerated. The acid is recovered by distillation before generating a slurry of metal salts. Plutonium removal can be performed before the distillation process. Silver recovery has been demonstrated from inactive wastes and this can be performed for active liquors if this is deemed economic

Objective 7 - The system shall require minimal off gas control processes and monitoring instruments

The process produces the following gases:

- Oxygen (anolyte only)
- Carbon dioxide (anolyte only)
- Carbon monoxide (anolyte only)
- Nitrous Oxide (anolyte only)
- Nitric Oxide (catholyte mainly, traces from anolyte)
- Nitrogen Dioxide (catholyte mainly, traces from anolyte)

The core process does not require gas analysis for control purposes. Control is based around liquid analysis.

Objective 8 - For decontamination systems -The system shall attain a minimal decontamination factor of 100

The system has attained a surrogate DF of 64. There were no visible signs of the copper oxalate contaminant of the test materials. This corresponds to 98.4% decontamination, which is very close to the target 99% decontamination.

Objective 9 - In addition, the data generated should enable scale-up estimates to be performed

The data required for scale-up estimates is:

The rate of decontamination	A 60A electrochemical cell operating in tandem with a 150W swept ultrasonic anolyte vessel can decontaminate ~20g of waste per hour
The rate of organic destruction (current efficiency)	From the molecular formula, we can calculate the treatment rate. A 60A electrochemical cell operating in tandem with a 150W-swept ultrasonic anolyte vessel can destroy 8.08g per hour. This corresponds to a current efficiency of 100%. The same value was calculated for test 9 during which the maximum destruction rate was 6.27g per hour of a mixture of rubber, nylon and oil
The rate of liquid transfers across the ceramic membrane	Liquid transfers can be controlled by appropriate use of flow controllers and level sensors
The rate of silver transfer across the ceramic membrane	There is a transfer of silver from anolyte to catholyte that corresponds to 1.6% of the measured current (0.038 moles per hour for a 60A cell)
The nitric acid balance within the plant	The transfer of nitrate from catholyte to anolyte is controlled by ionic mobility (~0.37 moles per hour for a 60A cell) and losses to the gas phase is based upon the reduction of nitric acid to nitric oxide (~0.7 moles per hour for a 60A cell)

Plant scale estimates.

Amount of waste		
Number of drums	5500	
Amount in drum	25	kg
Proportion of cellulose	45%	(assumed will be decontaminated and destroyed)
Total	61875	kg in total cellulose
Proportion of non-cellulose	55%	(assumed will be decontaminated)
Total	75625	kg in total non-cellulose
Rate of treatment		
Period	2	years
	104	weeks
Availability	80%	
	83	weeks
1 week	40	hours
Total hours	3328	hours
Rate of treatment	18.59	kg/h for cellulose
Rate of treatment	22.72	kg/h for non-cellulose
Rate of treatment	41.32	kg/h for drum contents
Results		
150W swept ultrasonic anolyte vessel was able to decontaminate 158g of waste within an eight hour period (~20g per hour).		
The maximum rate of cellulosic/nylon destruction (for this weight and type of waste) can be estimated to be ~8g per hour.		

Cell size calculations for destruction		
Rate of destruction @ 60A	0.008	kg/h
Current required for 1kg/h	7500	A
Rate required	18.59	kg/h for cellulose
Current required for this rate	139442	A
Current required for this rate	139.46	kA
Cell size calculations for decontamination		
Rate of decontamination @ 60A	0.02	kg/h
Current required for 1kg/h	3000	A
Rate required	41.32	kg/h for cellulose
Current required for this rate	123960	A
Current required for this rate	123.96	kA

Conclusion

Destruction is the rate limiting step and will require a cell capacity of 140 kA. A price of \$5M has been estimated for this type of plant for a Nuclear Environment. This price has been derived using the data from the inactive trials and is, as such, only a preliminary estimate. This price does not constitute a formal offer and should only be used for budgetary purposes.

6 References

1. 20 3067 01 07 Phase I Feed Preparation
2. 20 3067 01 12 SRS SILVER II Plant Manual
4. Demonstration II Final Report for PMACWA– May 2001–by AEAT/CH2MHill

7 Bibliography

No documents.

8 Acronyms and abbreviations

A	Amperes
AnalaR	Analytical grade reagent
C	Celsius
DC	Direct current
DF	Decontamination factor
EOR	End of run
FM	Flow module
g	Grams
HEPA	High efficiency particle attrition
ID	Identification number
I-TEQ	Toxic equivalent
M	mole litre-1
MEO	Mediated electrochemical oxidation
mg	milligram
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
PE	Polyethylene
PMACWA	Project Manager for Assembled Chemical Weapons Assessment
PS	Polystyrene
PUREX	Plutonium recovery and extraction
PVC	Polyvinylchloride
PVDF	Polyvinylidenedifluoride
RTV	Silicone based adhesive
SOR	Start of run
SOW	Statement of work
SRTC	Savannah River Site Technical Center
TBP	Tri-n-butylphosphate
TOC	Total organic carbon
US	Ultrasonic
USDOE	United States Department of Energy

V	Volts
W	Watts
WG	Water gauge
WIPP	Waste isolation pilot plant

Appendices

CONTENTS

Appendix 1	Analytical Methods
Appendix 2	Raw data
Appendix 3	Photographs
Appendix 4	Interpreted data

Appendix 1

Analytical Methods

CONTENTS

Method 1	Silver in solution
Method 2	Copper in solid samples
Method 3	Acid in solution
Method 4	TOC in solution

**ANALYTICAL METHOD FOR THE DETERMINATION OF
Silver In Sample
Ion Selective Electrode Titration**

APPROVED:

4/11/00

Task Manager

Date

4/11/00

Team Leader

Date

1.0 Scope and Application

- 1.1 This method is applicable to analysis of silver ions in anolyte or catholyte (both containing high concentrations of nitric acid).
- 1.2 Silver ions are analyzed by titration with potassium iodide and the iodide concentration followed by an ion selective electrode. The electrode is part of an auto-titrator system (Mettler DL25).
- 1.3 The ISE is an ion-selective detector that responds to the presence of iodide. If silver is present then the iodide is removed from the solution by precipitation as silver iodide. Once there is no more silver present then the iodide remains in solution and is detected by the electrode. A titration end point is identified by a rapid change in the electrode potential. The auto-titrator is able to recognize the end-point and then calculate the concentration of silver in the solution.
- 1.4 The method detection limits (MDL) for the silver have been artificially set at 0.1M. The technique is readily able to detect much smaller concentrations, but this is not necessary for this project.
- 1.5 Interferences
 - 1.5.1 Other metals with extremely insoluble iodides, such as lead.

2.0 Summary of the Method

- 2.1 Liquid sample to be analyzed from plant is taken and 0.1 ml is placed into the sample cup with 50 ml of deionised water.
- 2.2 The titrator adds potassium iodide to the sample and the end point is identified automatically as a point of inflexion.
- 2.3 The titrator then calculates the silver concentration by noting the total volume of iodide added and using values such as sample volume and iodide concentration that have been entered by the user.
- 2.4 The results are provided in the form of a printout.

3.0 Apparatus and Materials

- 3.1 Mettler DL25
- 3.2 ISE Iodide selective from Orion such as 9453BNC
- 3.3 Sample transfer - Gilson auto-pipette
- 3.4 Solutions
 - 3.4.1 Deionised water
 - 3.4.2 0.1M potassium iodide solution (16.601g KI in 1 liter of solution).
- 3.5 Calibration standard
 - 3.5.1 Stock Standard—Stock standard contain:
 - 3.5.1.1 1M AgNO_3 (169.780g AgNO_3 , ~8M HNO_3 (500 ml) made up to 1 liter of solution) from which we make up:
 - 3.5.1.2 0.5M AgNO_3 8M HNO_3

- 3.5.1.3 0.2M AgNO₃ 8M HNO₃
- 3.5.1.4 0.1M AgNO₃ 8M HNO₃
- 3.5.1.5 8M HNO₃

4.0 Initial Calibration

- 4.1 **Initial Calibration** — The analytical system is initially calibrated using five concentrations ranging from 0 to 1 M for all silver.
- 4.2 Calibrations are performed by an addition of the solution to the sample container. The square of the correlation coefficient (R^2) must be greater than 0.995 in order for the calibration to be considered acceptable. Initial calibrations are performed whenever the continuing calibration does not meet acceptable criteria.

5.0 Quality Assurance

- 5.1 **Method Blanks** —The analytical system must be demonstrated to be free from contamination by the analysis of a method blank. Method blank is performed by analysis of a 100 µL injection of nitric acid. Frequency of analysis is daily and before analysis of any calibration or field samples. Silver in the method blank must not be detected at concentrations above the reporting limit. If the method blank exceeds the criteria appropriate corrective actions must be taken and documented before further sample analysis.
- 5.2 **Continuing Calibration** —The working calibration curve and instrument response are verified by the analysis of a 100 µL injection of the stock standard. The frequency of analysis is once per 24-hour period or once per 20 samples. Control limits for analyte recovery is 80% to 120%.
- 5.3 **Duplicate Analysis** — Duplicate analyses are performed to verify the reproducibility of sample results. A duplicate analysis is performed once a day or one per 20 samples. The acceptance criteria for duplicate analysis is RPD<20. If this is not met, corrective action must be taken.

6.0 Procedure

- 6.1.1 Ensure the reagent bottle is reasonably full. Shake the bottle if condensation is present. Normally the reagent used is 0.1 M sodium hydroxide.
- 6.1.2 Ensure the burette lines have no air pockets in them. It is advisable to flush the lines and burette with reagent using the 'BURET ml' key if the titrator has not been in use for a few hours. One press of the key will flush 20 cc through the burette.
- 6.1.3 When finished flushing, dispose of the flushings and wash the titration cup and the electrode with demineralised water.
- 6.1.4 Add approximately 50 cc of demineralised water to the titration cup.
- 6.1.5 Add 0.1 cc of sample to the titration cup using a suitable pipette and screw the titration cup to the electrode assembly.
- 6.1.6 Check the number of the method currently being used by pressing the 'METHOD' key. Normally method 3 is used for acid determination but if

method 'no. 3' is not shown on the display then press '3' followed by 'METHOD' to recall it. Check that the correct concentration of the reagent has been entered in the method by pressing 'CONC'. If not then enter the reagent concentration and press 'CONC'. Details of method 3 are presented in appendix one. The entry or changing of method parameters is covered in more detail by the DL25 Operating Manual, which must be available to all operators.

- 6.1.7 Press 'RUN' on the keyboard. The 'weight' indicator will illuminate requesting the aliquot size.
 - 6.1.8 Press '0.1' then 'RUN'. The 'Ident' indicator will illuminate requesting the sample, or control, identity number.
 - 6.1.9 Enter 'Sample Identity' and press 'RUN'. The 'Busy' indicator will illuminate.
 - 6.1.10 Press 'RUN'. The titration will begin, the stirrer will rotate, and a millivolt reading, which corresponds to the cell voltage, will appear on the display. If a problem occurs simply press 'RESET' to stop the titration and return to the stand-by mode.
 - 6.1.11 The end point of the titration is signified by a large change in the cell voltage. The titration will stop and the result in molarity of acid will be displayed on the titrator and will also be printed out if a printer is connected.
 - 6.1.12 Enter the result in the logbook beside the sample identity number.
 - 6.1.13 Empty the titration cup into a suitable waste container and wash the cup and electrode with demineralised water. DO NOT PUT SILVER BEARING WASTE SOLUTIONS DOWN THE DRAIN. Proceed to step 4 for the next sample.
 - 6.1.14 If no further analyses are required then fill the titration cup with approximately 50 cc of demineralised water and screw the titration cup to the electrode assembly and leave until required for further analyses.
- 6.2 Instrumental Operating Conditions (see section 6.1)
- 6.2.1 METHOD 3 Parameters
 - 6.2.1.1 conc mol/l0.1000this is the reagent concentration
 - 6.2.1.2 const reag1.0000conversion factor for the reagent concentration
 - 6.2.1.3 back m/mol0.0000excess of titrant for back titrations
 - 6.2.1.4 blank m/mol0.0000consumption of titrant in blank titration
 - 6.2.1.5 const1.0000calculation constant for units
 - 6.2.2 CONFIGURATION
 - 6.2.2.1 1 TYPE0001standard mode; min increment 1% of 20 cc; measured variable = mv; titration to the equivalence point
 - 6.2.2.2 2 CONTROL1001drift 1mv; time min = 1.5 s; max = 20 s
 - 6.2.2.3 voltage change = 8 mv; max increment = 2% burette vol

- 6.2.2.4 3 PREDOSING 0.5 standard volume 0.5 cc predisposed
- 6.2.2.5 4 BUR/MAXVOL 1020 burette vol. = 20 cc; max vol. = 20 cc
- 6.2.2.6 5 END-POINT 0 standard dosing threshold
- 6.2.2.7 6 STIR TIME 10 stirring time before start in seconds
- 6.2.2.8 7 OUTPUT 810 initial signal mv; consumption in cc; no curve
- 6.2.2.9 8 SYSTEM 1 dot-matrix printer
- 6.2.2.10 9 SERIES 0 sample data input
- 6.2.2.11 A0 rinsing time in seconds for series titrations
- 6.2.2.12 B0 dosing time in seconds for series titrations with pump at
- 6.2.2.13 RINSE
- 6.2.2.14 C0 dosing time in seconds for series titrations with pump at DOSE

6.3 Data Calculation and Reporting

6.3.1 Data Calculation is performed by the instrument.

6.3.2 A rejection quotient Q is defined as

A rejection quotient Q is defined as

$$Q = (x_n - x_{n-1}) / (x_n - x_1)$$

where x_n is the questionable result in a set $x_1, x_2, x_3, \dots, x_n$

Q is calculated and compared with a table of critical values below. The result is rejected if

$$Q (\text{experimental}) > Q (\text{critical})$$

Number of results	Q (critical) level	90% confidence level
2		-
3		0.94
4		0.76
5		0.64
6		0.56
7		0.51
8		0.47
9		0.44

1. Fifield & Kealey " Principles and Practice of Analytical Chemistry "
2nd Ed. ITC

- 6.3.3 Laboratory Reports - Field sample results can be reported in three quality control (QC) levels. A level 1 report is a summary of client sample results only. A level 2 report includes a summary of client sample results along with method blank, initial calibration, continuing calibration, and duplicate analysis results. Instrument printouts are not included in a level 2 report. A level 3 report includes all documentation submitted in a level 2 report plus instrument printouts.

**ANALYTICAL METHOD FOR THE DETERMINATION OF
Metals in solids**

Ashing/Digestion/Atomic Absorption

APPROVED:

4/11/00

Task Manager

Date

4/11/00

Team Leader

Date

1.0 Scope and Application

- 1.1 This method is applicable to analysis of metals in organic or metals samples that can be solubilized by ashing at 800C followed by aqua regia digestion.
- 1.2 Metals are analyzed by atomic absorption spectroscopy (Perkin Elmer 2380).
- 1.3 Post dissolution, the liquor may need to be diluted to provide samples that can be readily analyzed using the 2380 instrument.
- 1.4 The method detection limits (MDL) for the metals analysis have been set to those of the 2380 for the specific metal. The technique is able to detect much smaller concentrations, but this involves further sample preparation - such as either solvent extraction or evaporation.
- 1.5 Interferences
 - 1.5.1 The primary interferences are identified in the 2380 operations manual. Matrix effects should be considered during analysis.

2.0 Summary of the Method

- 2.1 The solid sample to be analyzed from plant is taken and is placed onto the quartz ashing tray.
- 2.2 The tray and sample are placed into the furnace and the temperature raised to 800C over a 1 hour period.
- 2.3 The tray and sample are left in the furnace for 2 hours.
- 2.4 The furnace is switched off and allowed to cool by natural convection.
- 2.5 The tray is taken and 75mls of aqua regia (1:3 concentrated HNO_3 :HCl) is added. The solution is boiled using a hotplate and allowed to evaporate to dryness.
- 2.6 The tray is taken and a further 25mls of aqua regia (1:3 concentrated HNO_3 :HCl) is added. The solution is boiled but not allowed to evaporate to dryness.
- 2.7 The solution and remaining solids are transferred to a beaker and the tray is rinsed with deionised water and the aqua regia and water are combined.
- 2.8 The solids/liquid mixture is filtered through a Whatman GF filter and the filtrate is kept for analysis.
- 2.9 The tray is taken and a further 25mls of aqua regia (1:3 concentrated HNO_3 :HCl) is added. The solution is boiled but not allowed to evaporate to dryness.
- 2.10 The solution is transferred to a beaker and the tray is rinsed with deionised water and the aqua regia and water are combined.
- 2.11 The samples are analyzed for the appropriate metal using the Perkin Elmer 2380 as per the operating manual.

3.0 Apparatus and Materials

- 3.1 Quartz tray
- 3.2 Standard laboratory hot plate

- 3.3 Laboratory furnace capable of operating at 800C with the quartz tray
 - 3.4 Perkin Elmer 2380 atomic absorption spectrometer
 - 3.5 Oertling GC 62 laboratory balance
 - 3.6 Standard grade volumetric laboratory glassware
 - 3.7 Solutions
 - 3.7.1 Deionised water
 - 3.7.2 AnalaR grade concentrated nitric acid
 - 3.7.3 AnalaR grade concentrated hydrochloric acid
 - 3.7.4 Gases/Reagents as specified in the 2380 Manual (including calibration standards)
- 4.0 **Initial Calibration**
 - 4.1 **Initial test** —The process is evaluated by performing three ashing/digestion tests with a sample of the target material.
 - 4.2 Calibration of the 2380 is performed using 4 standards (one a blank) that are prepared on the day of analysis using a commercially available standard solution. Initial calibrations are performed whenever the continuing calibration (every 20 samples or at the start of an analysis batch) does not meet acceptable criteria.
- 5.0 **Quality Assurance**
 - 5.1 **Method Blanks** — The analytical system must be demonstrated to be free from contamination by the analysis of a method blank. Method blank is performed by analysis of a 100 µL injection of water. Frequency of analysis is daily and before analysis of any calibration or field samples. Metals in the method blank must not be detected at concentrations above the 2380 reporting limit for the specific metal. If the method blank exceeds the criteria appropriate corrective actions must be taken and documented before further sample analysis.
 - 5.2 **Continuing Calibration** —The working calibration curve and instrument response are verified by the analysis of the mid-range standard. The frequency of analysis is once per 24-hour period or once per 20 samples. Control limits for analyte recovery is 80% to 120%.
 - 5.3 **Duplicate Analysis** — Duplicate analyses are performed to verify the reproducibility of sample results. A duplicate analysis is performed once a day or one per 20 samples. The acceptance criteria for duplicate analysis is RPD<20. If this is not met, corrective action must be taken.
- 6.0 **Procedure**
 - 6.1 The quartz tray should be dried in an oven at 100°C for 2 hours and allowed to cool to room temperature before weighing.
 - 6.2 The solid sample to be analyzed from plant is taken and is placed onto the quartz ashing tray.
 - 6.3 The tray and samples are reweighed.

- 6.4 The tray and sample are placed into the furnace and the temperature raised to 800C over a 1 hour period.
- 6.5 The tray and sample are left in the furnace for 2 hours.
- 6.6 The furnace is switched off and allowed to cool by natural convection.
- 6.7 The tray are charred samples are reweighed.
- 6.8 The tray is taken and 75mls of aqua regia (1:3 concentrated $\text{HNO}_3:\text{HCl}$) is added. The solution is boiled gently by placing the tray onto a hotplate. The liquor is allowed to evaporate to dryness.
- 6.9 The tray is taken and a further 25mls of aqua regia (1:3 concentrated $\text{HNO}_3:\text{HCl}$) is added. The solution is boiled but not allowed to evaporate to dryness.
- 6.10 The solution and remaining solids are transferred to a beaker and the tray is rinsed with 25mls of deionised water and the aqua regia and water are combined.
- 6.11 The solids/liquid mixture is filtered through a Whatman GF filter and the filtrate is kept for analysis. The volume is recorded.
- 6.12 The tray is taken and a further 25mls of aqua regia (1:3 concentrated $\text{HNO}_3:\text{HCl}$) is added. The solution is boiled but not allowed to evaporate to dryness.
- 6.13 The solution is transferred to a beaker and the tray is rinsed with deionised water and the aqua regia and water are combined. The volume is recorded.
- 6.14 The samples are analyzed for the appropriate metal using the Perkin Elmer 2380 as per the operating manual.
- 6.15 Data Calculation and Reporting

6.15.1 Data Calculation is performed by the instrument.

6.15.2 A rejection quotient Q is defined as

A rejection quotient Q is defined as

$$Q = (x_n - x_{n-1}) / (x_n - x_1)$$

where x_n is the questionable result in a set $x_1, x_2, x_3, \dots, x_n$

Q is calculated and compared with a table of critical values below. The result is rejected if

$$Q (\text{experimental}) > Q (\text{critical})$$

Number of results	Q (critical) 90% confidence level
2	-
3	0.94
4	0.76
5	0.64

	6	0.56
7		0.51
8		0.47
9		0.44
10		0.41

1. Fifield & Kealey 'Principles and Practice of Analytical Chemistry'
2nd Ed. ITC

6.15.3 Laboratory Reports - Field sample results can be reported in three quality control (QC) levels. A level 1 report is a summary of client sample results only. A level 2 report includes a summary of client sample results along with method blank, initial calibration, continuing calibration, and duplicate analysis results. Instrument printouts are not included in a level 2 report. A level 3 report includes all documentation submitted in a level 2 report plus instrument printouts.

**ANALYTICAL METHOD FOR THE DETERMINATION OF
Acidity In Sample
pH Electrode Titration**

APPROVED:

4/11/00

Task Manager

Date

4/11/00

Team Leader

Date

1.0 Scope and Application

- 1.1 This method is applicable to analysis of acidity in anolyte or catholyte (both containing high concentrations of nitric acid).
- 1.2 Acidity is analyzed by titration with sodium hydroxide and the H_3O^+ concentration followed by a pH sensitive electrode. The electrode is part of an auto-titrator system (Mettler DL25).
- 1.3 The pH electrode has a logarithmic response to acidity. As hydroxide is added so the pH rises and the electrode measures this rise. A very rapid change in pH occurs around pH7 for titration systems operating with a strong acid and a strong base. This point of inflexion is measured as the end-point of the titration. The auto-titrator is able to recognize the end-point and then calculate the concentration of acid in the solution.
- 1.4 The method detection limits (MDL) for the acidity have been artificially set at 0.5M. The technique is readily able to detect much smaller concentrations, but this is not necessary for this project.
- 1.5 Interferences
 - 1.5.1 Other acids and materials that result in precipitates upon reaction with hydroxide.

2.0 Summary of the Method

- 2.1 Liquid sample to be analyzed from plant is taken and 0.1 ml is placed into the sample cup with 50 ml of deionised water.
- 2.2 The titrator adds sodium hydroxide to the sample and the end point is identified automatically as a point of inflexion.
- 2.3 The titrator then calculates the acid concentration by noting the total volume of titrant added and using values such as sample volume and hydroxide concentration that have been entered by the user.
- 2.4 The results are provided in the form of a printout.

3.0 Apparatus and Materials

- 3.1 Mettler DL25
- 3.2 pH electrode from Orion such as PerphecT ROSS pH Combination with Epoxy Body, Flat Surface
- 3.3 Sample transfer - Gilson auto-pipette
- 3.4 Solutions
 - 3.4.1 Deionised water
 - 3.4.2 0.1M sodium hydroxide solution (made up from ConVol standard available from Merck BDH)
- 3.5 Calibration standard
 - 3.5.1 Stock Standard—Stock standard contain:
 - 3.5.1.1 8M HNO_3 (500 ml) made up to 1 liter of solution) from which we make up:

- 3.5.1.2 2M HNO₃
- 3.5.1.3 1M HNO₃
- 3.5.1.4 0.1M AgNO₃ 8M HNO₃
- 3.5.1.5 0M HNO₃

4.0 Initial Calibration

- 4.1 **Initial Calibration** —The analytical system is initially calibrated using five concentrations ranging from 0 to 8 M for all acid.
- 4.2 Calibrations are performed by an addition of the solution to the sample container. The square of the correlation coefficient (R^2) must be greater than 0.995 in order for the calibration to be considered acceptable. Initial calibrations are performed whenever the continuing calibration does not meet acceptable criteria.

5.0 Quality Assurance

- 5.1 **Method Blanks** —The analytical system must be demonstrated to be free from contamination by the analysis of a method blank. Method blank is performed by analysis of a 100 µL injection of water. Frequency of analysis is daily and before analysis of any calibration or field samples. Acid in the method blank must not be detected at concentrations above the reporting limit. If the method blank exceeds the criteria appropriate corrective actions must be taken and documented before further sample analysis.
- 5.2 **Continuing Calibration** —The working calibration curve and instrument response are verified by the analysis of a 100 µL injection of the stock standard. The frequency of analysis is once per 24-hour period or once per 20 samples. Control limits for analyte recovery is 80% to 120%.
- 5.3 **Duplicate Analysis** — Duplicate analyses are performed to verify the reproducibility of sample results. A duplicate analysis is performed once a day or one per 20 samples. The acceptance criteria for duplicate analysis is RPD<20. If this is not met, corrective action must be taken.

6.0 Procedure

- 6.1 Method
 - 6.1.1 Call up method 3 on the DL25 memotitrator . This is the saved method used for hydroxide determination. This is achieved by pressing '3' followed by 'METHOD'.
 - 6.1.2 Using a known acid standard obtain a correct concentration for the 0.1M sodium hydroxide reagent which will be used for the titrations. Enter the correct concentration by entering the figure followed by 'CONC'. The 'CONST REAG' figure can then be entered. This is a factor that converts the reagent concentration to the desired concentration.
 - 6.1.3 Add 50 cc of demineralised water to the titration cup.
 - 6.1.4 Add 0.1cc of the acid solution, when it has reached an ambient temperature, to titration cup.
 - 6.1.5 Screw the titration cup to the electrode assembly.

- 6.1.6 Check the number of the method currently being used by pressing the 'METHOD' key. If method 'no. 3' is not shown on the display then press '3' followed by 'METHOD' to recall it. Check that the correct concentration of reagent has been entered in the method by pressing 'CONC'. Details of method 3 are presented later.
- 6.1.7 Press 'RUN'. The 'weight' indicator will illuminate requesting the aliquot size.
- 6.1.8 Press '0.1' then 'RUN'. The 'Ident' indicator will illuminate requesting the sample, or control, identity number.
- 6.1.9 Enter 'Sample Identity' and press 'RUN'. The 'Busy' indicator will illuminate.
- 6.1.10 Press 'RUN'. The titration will begin, the stirrer will rotate, and a millivolt reading, which corresponds to the cell voltage, will appear on the display.
- 6.1.11 If a problem occurs simply press 'RESET' to stop the titration and return to the stand-by mode.
- 6.1.12 The end-point of the titration is signified by a large change in the cell voltage. The titration will stop and the result in molarity(M) of acid will be displayed and will also be printed out if a printer is connected.
- 6.1.13 Enter the result in the logbook beside the sample identity.
- 6.1.14 Empty the titration cup into a suitable waste container and wash the electrode and cup with demineralised water.
- 6.1.15 If no further analyses are required then fill the titration cup with approximately 50cc of demineralised water and screw the titration cup to the electrode assembly and leave until required for further analyses.
- 6.2 Instrumental Operating Conditions (see section 6.1)
 - 6.2.1 METHOD 3 Parameters
 - 6.2.1.1 conc mol/l 0.1000 this is the reagent concentration
 - 6.2.1.2 const reag 1.0000 conversion factor for the reagent concentration
 - 6.2.1.3 back m/mol 0.0000 excess of titrant for back titrations
 - 6.2.1.4 blank mmol 0.0000 consumption of titrant in blank titration
 - 6.2.1.5 const 1.0000 calculation constant for units
 - 6.2.2 CONFIGURATION
 - 6.2.2.1 TYPE 0001 standard mode; min increment 1% of 20 cc; measured variable = mv; titration to the equivalence point
 - 6.2.2.2 CONTROL 1001 drift 1mv ; time min = 1.5 s; max = 20 s voltage change = 8 mv; max increment = 2% burette vol
 - 6.2.2.3 PREDOSING 0.5 standard volume 0.5 cc predispensed
 - 6.2.2.4 BUR/MAXVOL 1020 burette vol. = 20 cc; max vol. = 20 cc

- 6.2.2.5 END-POINT 0 standard dosing threshold
- 6.2.2.6 STIR TIME 10 stirring time before start in seconds
- 6.2.2.7 OUTPUT 810 initial signal mv; consumption in cc; no curve
- 6.2.2.8 SYSTEM 1 dot-matrix printer
- 6.2.2.9 SERIES 0 sample data input
- 6.2.2.10 0 rinsing time in seconds for series titrations
- 6.2.2.11 0 dosing time in seconds for series titrations with pump at
- 6.2.2.12 RINSE
- 6.2.2.13 0 dosing time in seconds for series titrations with pump at DOSE
- 6.2.2.14 conc mol/l0.1000 this is the reagent concentration
- 6.2.2.15 const reag1.0000 conversion factor for the reagent concentration
- 6.2.2.16 back m/mol0.0000 excess of titrant for back titrations
- 6.2.2.17 blank m/mol0.0000 consumption of titrant in blank titration
- 6.2.2.18 const 1.0000 calculation constant for units

6.3 Data Calculation and Reporting

6.3.1 Data Calculation is performed by the instrument.

6.3.2 A rejection quotient Q is defined as

A rejection quotient Q is defined as

$$Q = (x_n - x_{n-1}) / (x_n - x_1)$$

where x_n is the questionable result in a set $x_1, x_2, x_3, \dots, x_n$

Q is calculated and compared with a table of critical values below. The result is rejected if:

$$Q (\text{experimental}) > Q (\text{critical})$$

Number of results	Q (critical) level	90% confidence
2	-	
3	0.94	
4	0.76	
5	0.64	
6	0.56	
7	0.51	
8	0.47	
9	0.44	
10	0.41	

1. Fifield & Kealey 'Principles and Practice of Analytical Chemistry' 2nd Ed. ITC

- 6.3.3 Laboratory Reports - Field sample results can be reported in three quality control (QC) levels. A level 1 report is a summary of client sample results only. A level 2 report includes a summary of client sample results along with method blank, initial calibration, continuing calibration, and duplicate analysis results. Instrument printouts are not included in a level 2 report. A level 3 report includes all documentation submitted in a level 2 report plus instrument printouts.

**ANALYTICAL METHOD FOR THE DETERMINATION OF
TOC**

Modified Hach Method

APPROVED:

4/6/02

Task Manager

Date

4/6/02

Team Leader

Date

1.0 **Scope and Application**

- 1.1 This method is based upon Hach method 10128.
- 1.2 The modification is that custom built Hach spectrophotometer is replaced by a Cecil 599 scanning UV/Vis spectrophotometer.
- 1.3 The range of the analysis is 100-700 mg/l TOC. Samples with TOC values greater than 700 mg/l should be repeated. Care should be taken when evaluating data from samples with TOC values less than 100 mg/l.
- 1.4 The method is based upon acidic persulphate oxidation with simultaneous CO₂ absorption into a pH sensitive dye. Visible spectrophotometry is used to determine the concentration of the TOC.
- 1.5 Interferences are as per Hach method 10128.

2.0 **Summary of the Method**

- 2.1 Persulphate powder is added to the sample tube that already contains sulfuric acid.
- 2.2 Liquid sample to be analyzed from plant is taken and 0.3 ml is placed into the sample tube and mixed by gentle swirling of the solids by using a circular motion.
- 2.3 The vial containing the dye is cleaned with deionised water and dried using a lint free tissue.
- 2.4 The dye vial is placed into the test tube and the top of the tube removed (the vial is pre-marked to facilitate this action).
- 2.5 The lid is placed firmly on the tube.
- 2.6 The tube is placed in a heating mantle at 103-105C.
- 2.7 The tube is removed from the mantle and allowed to cool for one hour.
- 2.8 1ml of the solution from the dye vial is removed by Pasteur pipette and placed into quartz cuvette.
- 2.9 The cuvette is placed into the spectrophotometer and the absorbance measured at 430 and 598nm.

3.0 **Apparatus and Materials**

- 3.1 Hach kit 10128.
- 3.2 Heating mantle with metal block with holes that can accommodate the test tube.
- 3.3 Pasteur pipette.
- 3.4 UV/Vis spectrophotometer capable of measuring at 430 and 598nm.
- 3.5 Matched quartz cuvettes (or cuvettes against which the blank absorbencies have been determined at the appropriate wavelengths).
- 3.6 Deionised water.
- 3.7 Calibration standard. (1000 mg/l TOC stock prepared from 2.1254g potassium hydrogen phthalate made up to 1 liter using organic free deionised water.

Standards of varying concentrations can be prepared from this solution by dilution in organic free deionised water).

4.0 Initial Calibration

- 4.1 **Initial Calibration**—The analytical system is initially calibrated using three concentrations ranging from 100, 200 and 300 mg/l TOC prepared from the stock solution.
- 4.2 Calibrations are performed by an addition of the solution to the sample container. The square of the correlation coefficient (R^2) must be greater than 0.995 in order for the calibration to be considered acceptable. Initial calibrations are performed whenever the continuing calibration does not meet acceptable criteria.

5.0 Quality Assurance

- 5.1 **Method Blanks** —The analytical system must be demonstrated to be free from contamination by the analysis of a method blank. Method blank is performed by analysis of a 300 µL injection of water. Frequency of analysis is daily and before analysis of any calibration or field samples. TOC in the method blank must not be detected at concentrations above the reporting limit. If the method blank exceeds the criteria appropriate corrective actions must be taken and documented before further sample analysis.
- 5.2 **Continuing Calibration** —The working calibration curve and instrument response are verified by the analysis of a 300 µL injection of the standard. The frequency of analysis is once per 24-hour period or once per 20 samples. Control limits for analyte recovery is 80% to 120%.
- 5.3 **Duplicate Analysis** — Duplicate analyses are performed to verify the reproducibility of sample results. A duplicate analysis is performed once a day or one per 20 samples. The acceptance criteria for duplicate analysis is $RPD < 20$. If this is not met, corrective action must be taken.

6.0 Procedure

- 6.1 Method
 - 6.1.1 Take the Hach tube and remove the lid.
 - 6.1.2 Add persulphate powder from the chemical pillow to the sample tube that already contains sulfuric acid. Discard the empty pillow in a suitable waste container.
 - 6.1.3 Liquid sample to be analyzed from plant is taken and 0.3 ml is placed into the sample tube using a Gilson pipette and the contents are mixed by a gentle swirling of the solids and solution by using a circular motion of the tube.
 - 6.1.4 The vial containing the dye is cleaned with deionised water and dried using a lint free tissue. Do not handle the tube below the marked line (this is a nick mark that will be used to crack the tube in a controlled fashion).
 - 6.1.5 The cleaned dye-vial is placed carefully into the test tube so that the top of the vial above the mark is outside of the tube. The top of the vial

is removed (the vial is pre-marked to facilitate this action) by carefully holding the top of the vial and snapping it off along the pre-marked nick (do not shake).

6.1.6 The lid is placed firmly on the tube (do not shake).

6.1.7 The tube is placed in a heating mantle that has been preheated to between 103-105C.

6.1.8 The tube is left in place for 2 hours.

6.1.9 The tube is removed from the mantle (careful, hot) and allowed to cool in a vertical position for one hour (do not shake).

6.1.10 1ml of the solution from the dye vial is removed by Pasteur pipette and placed into a cleaned and dry quartz cuvette.

6.1.11 The cuvette is placed into the spectrophotometer and the absorbance measured at 430 and 598nm.

6.2 UV/Vis Operation

6.2.1 Set-up

6.2.1.1 Read the work instruction beside the instrument.

6.2.1.2 Switch on the UV/Vis and set to absorbance with a full scale setting of 1.

6.2.1.3 Allow to equilibrate for at least twenty minutes.

6.2.1.4 Take the quartz cuvettes and ensure that neither are marked or dirty. If marked then clean using acetone followed by organic free deionised water.

6.2.1.5 Fill both cuvettes with deionised water and place into the spectrophotometer.

6.2.1.6 Set the wavelength to 430 nm and use the coarse and fine adjusts to produce an absorbance of zero.

6.2.1.7 Change the wavelength to 589nm and measure and record the absorbance.

6.2.1.8 Drain the sample cuvette (closest to the operator) and dry with a non-lint containing tissue.

6.2.1.9 Rinse the cuvette with 0.2ml of the sample to be analyzed using a pipette and drain but do not dry.

6.2.1.10 Place ~1ml of sample into the cuvette using a pipette.

6.2.1.11 Place the cuvette in the spectrophotometer sample position and measure the absorbance at 589nm and then at 430nm.

6.2.1.12 Drain the sample from the cuvette and dry with a non-lint containing tissue.

6.2.1.13 Repeat steps 6.2.1.10 to 6.2.1.12 using the next sample.

6.2.1.14 Once the analyses are complete then rinse the cuvette with deionised water twice before drying with a non-lint containing tissue.

6.2.1.15 Switch off the instrument.

6.3 Data Calculation and Reporting

6.3.1 Data Calculation is performed by the instrument.

6.3.2 A rejection quotient Q is defined as

A rejection quotient Q is defined as

$$Q = (x_n - x_{n-1}) / (x_n - x_1)$$

where x_n is the questionable result in a set $x_1, x_2, x_3, \dots, x_n$

Q is calculated and compared with a table of critical values below. The result is rejected if

$$Q (\text{experimental}) > Q (\text{critical})$$

Number of results	Q (critical) level	90% confidence
2		-
3		0.94
4		0.76
5		0.64
6		0.56
7		0.51
8		0.47
9		0.44
10		0.41

1. Fifield & Kealey 'Principles and Practice of Analytical Chemistry'
2nd Ed. ITC

6.3.3 Laboratory Reports--Field sample results can be reported in three quality control (QC) levels. A level 1 report is a summary of client sample results only. A level 2 report includes a summary of client sample results along with method blank, initial calibration, continuing calibration, and duplicate analysis results. Instrument printouts are not included in a level 2 report. A level 3 report includes all documentation submitted in a level 2 report plus instrument printouts.

Appendix 2

Data

CONTENTS

Tests 1-10

Test#	1	Copper oxalate $\text{Cu C}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	160.57 g/mole
			39.55% Cu by weight
Conditions		Start and end results	
Date	20/06/02	Copper oxalate in sample (start)	519.1 ma
Material	Mixed from customer	Copper in sample (start)	205.29 mg
Temperature	60 oC	Copper in sample (end)	31.85 mg
Anolyte	8M HNO_3 , 0.5M AgNO_3 (5l)	Copper in solution (end)	136.54 mg
Catholyte	8M HNO_3 (5l)	Weight of sample (start)*	51.0044 g
Current	60 A	Weight of sample (end)*	31 g
Ultrasound	0 W	*organics	20.0044 g
Duration	8 h		

Anolyte level to Volume conversion

slope 202.982

intercept 475.483

Catholyte level to Volume conversion

slope 238.529

intercept 226.349

Conclusions 57.70 in anolyte. 8.80 in catholyte. 15.51 in solids 82.02 total (DF 6.45)

Data section														
Physical parameters													Samples collected	
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte
		Watts	A	V	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)		Silver (M)
20-Jun	10:00	0	0	0	25	125	17.5	0.02	??	125	19.5	0.02	C036	C035
20-Jun	10:25	0	60	5	58	125	17.5	0.02	??	125	19.5	0.02	C038	C037
20-Jun	12:05	0	60	4.85	59	125	17.1	0.02	??	125	19.6	0.02	C040	C039
20-Jun	14:05	0	60	4.9	59	125	15.6	0.02	??	125	20.4	0.02	C042	C041
20-Jun	16:10	0	60	5.1	59	125	15.2	0.02	??	125	20.5	0.02	C044	C043
20-Jun	18:10	0	60	5	59	125	14.9	0.02	??	125	20.7	0.02	C046	C045

Test#	2	Copper oxalate $\text{Cu C}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	160.57 g/mole
			39.55% Cu by weight
Conditions		Start and end results	
Date	24/06/02	Copper oxalate in sample (start)	507.6 ma
Material	Mixed from customer	Copper in sample (start)	200.74 mg
Temperature	60 oC	Copper in sample (end)	32.4 mg
Anolyte	8M HNO_3 , 0.5M AgNO_3 (5l)	Copper in solution (end)	119.72 mg
Catholyte	8M HNO_3 (5l)	Weight of sample (start)*	50.0295 g
Current	60 A	Weight of sample (end)*	30.9 g
Ultrasound	100 W	*organics only	19.1295
Duration	8 h		

Anolyte level to Volume conversion

slope 202.982

intercept 475.483

Catholyte level to Volume conversion

slope 238.529

intercept 226.349

Conclusions 51.76 in anolyte. 7.88 in catholyte. 16.14 in solids 75.78 total (DF 6.20)

Data section															
Physical parameters													Samples collected		Analytical
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte	
		Watts	A	V	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)			Silver (M)
24-Jun	8:40	100	0	0	30	125	18.3	0.02 ??		125	19.2	0.02	D074	D073	0.5106
24-Jun	8:50	100	60	4.9	60	125	17.8	0.02 ??		125	18.8	0.02	D076	D075	0.4741
24-Jun	10:55	100	60	4.8	60	125	17.2	0.02 ??		125	19.4	0.02	D078	D077	0.4789
24-Jun	12:50	100	60	4.8	60	125	16.6	0.02 ??		125	19.9	0.02	D080	D079	0.4654
24-Jun	14:55	100	60	4.8	60	125	15.7	0.02 ??		125	20.7	0.02	D082	D081	0.4453
24-Jun	16:50	100	60	4.8	59	125	14.8	0.02 ??		125	20.8	0.02	D084	D083	0.452

Test# 3

Conditions
 Date 25/06/02
 Material Mixed from customer
 Temperature 80 oC
 Anolyte 8M HNO₃, 0.5M AgNO₃ (5l)
 Catholyte 8M HNO₃ (5l)
 Current 60 A
 Ultrasound 200 W
 Duration 8 h

Start and end results
 Copper oxalate in sample (start) 492.2 ma
 Copper in sample (start) 194.65 mg
 Copper in sample (end) 12.6 mg
 Copper in solution (end) 138.43 mg
 Weight of sample (start) 48.5626 a
 Weight of sample (end)1* 8.96 a
 Weight of sample (end)2* 16.25 a
 *organics ^ 23.3526 a
 2 cemented, 1 non-cemented

Anolyte level to Volume conversion

slope 202.982

intercept 475.483

Catholyte level to Volume conversion

slope 238.529

intercept 226.349

Conclusions 62.90 in anolyte. 8.22 in catholyte. 6.47 in solids 77.59 total (DF 15.45)

Data section															
Physical parameters													Samples collected		Analytical
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte	
		Watts	A	V	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)			Silver (M)
25-Jun	9:45	200	60	4.8	80	125	18.8	0.02 ??	125	17.7	0.02	C052	C053		0.5086
25-Jun	11:45	200	60	4.6	83	125	18.4	0.02 ??	125	17.7	0.02	C054	C055		0.488
25-Jun	13:55	200	60	4.5	83	125	17.7	0.02 ??	125	18.4	0.02	C057	C056		0.4852
25-Jun	15:50	200	60	4.5	82	125	16.7	0.02 ??	125	18.7	0.02	C058	C059		0.4781
25-Jun	17:42	200	60	4.5	82	125	15.7	0.02 ??	125	18.9	0.02	C060	C061		0.4796

Test#	4	Copper oxalate $\text{Cu C}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	160.57 g/mole
			39.55% Cu by weight
Conditions		Start and end results	
Date	27/06/02	Copper oxalate in sample (start)	496.5 ma
Material	Mixed from customer	Copper in sample (start)	196.35 mg
Temperature	45 oC	Copper in sample (end)	53.5 mg
Anolyte	8M HNO_3 , 0.5M AgNO_3 (5l)	Copper in solution (end)	142.22 mg
Catholyte	8M HNO_3 (5l)	Weight of sample (start)*	49.4189 g
Current	60 A	Weight of sample (end)*	33.8 g
Ultrasound	100 W	*organics	15.62 g
Duration	8 h		

Anolyte level to Volume conversion

slope 202.982

intercept 475.483

Catholyte level to Volume conversion

slope 238.529

intercept 226.349

Conclusions 59.26 in anolyte. 13.17 in catholyte. 27.25 in solids 99.68 total (DF 3.67)

Data section															
Physical parameters													Samples collected		Analytical
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte	
		Watts	A	V	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)			Silver (M)
27-Jun	9:45	100	60	4.8	40	125	17.7	0.02	??	125	15.2	0.02	C065	C064	0.4589
27-Jun	11:45	100	60	4.6	55	125	17.2	0.02	??	125	15.7	0.02	C067	C066	0.4393
27-Jun	13:55	100	60	4.5	56	125	16.2	0.02	??	125	16.5	0.02	C069	C068	0.4741
27-Jun	15:50	100	60	4.5	58	125	15.1	0.02	??	125	17.2	0.02	C071	C070	0.4209
27-Jun	17:42	100	60	4.5	58	125	14.2	0.02	??	125	17.8	0.02	C073	C072	0.429

Test# 5

Conditions

Date 01/07/02

Material Mixed from customer

Temperature 80 oC

Anolyte 8M HNO₃, 0.5M AgNO₃ (5l)

Catholyte 8M HNO₃ (5l)

Current 60 A

Ultrasound 0 W

Duration 8 h

Start and end results

Copper oxalate in sample (start) 508.5 ma

Copper in sample (start) 201.09 mg

Copper in sample (end) 53.5 mg

Copper in solution (end) 141.22 mg

Weight of sample (start) 48.4531 a

Weight of sample (end)1* 11.74 a

Weight of sample (end)2* 19.15 a

*organics ^ 17.5631 a

2 cemented, 1 non-cemented

Anolyte level to Volume conversion

slope 202.982

intercept 475.483

Catholyte level to Volume conversion

slope 238.529

intercept 226.349

Conclusions 66.80 in anolyte. 3.43 in catholyte. 26.60 in solids 96.83 total (DF 3.76)

Data section															
Physical parameters													Samples collected		Analytical
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte	
		Watts	A	V	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)			Silver (M)
1-Jul	9:50	0	60	4.9	80	125	16.2	0.02 ??	125	16.5	0.02	C083	C082		0.4648
1-Jul	11:25	0	60	4.8	70	125	16.3	0.02 ??	125	16.2	0.02	C085	C084		0.4697
1-Jul	13:25	0	60	4.8	74	125	16.1	0.02 ??	125	16.4	0.02	C087	C086		0.467
1-Jul	15:25	0	60	4.7	75	125	15.9	0.02 ??	125	16.3	0.02	C091	C090		0.4655
1-Jul	17:25	0	60	4.7	74	125	15.8	0.02 ??	125	16.8	0.02	C093	C092		0.449

Test# 6

Conditions

Date 03/07/02

Material Mixed from customer

Temperature 60 °C

Anolyte 8M HNO₃, 0.5M AgNO₃ (5l)

Catholyte 8M HNO₃ (5l)

Current 60 A

Ultrasound 150 W

Duration 8 h

Copper oxalate Cu C₂O₄ 0.5H₂O

Start and end results

Copper oxalate in sample (start) 503 mg

Copper in sample (start) 198.92 mg

Copper in sample (end) 53.5 mg

Copper in solution (end) 140.98 mg

Weight of sample (start) 50.0749 g

Weight of sample (end)1* 24.4 g

Weight of sample (end)2* 12.25 g

*organics 13.4249 g

2 cemented, 1 non-cemented

Anolyte level to Volume conversion

slope 202.982

intercept 475.483

Catholyte level to Volume conversion

slope 238.529

intercept 226.349

Conclusions 66.75 in anolyte. 4.12 in catholyte. 26.90 in solids 97.77 total (DF 3.72)

Data section														
Physical parameters													Samples collected	
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte
		Watts	A	V	Temp (°C)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (°C)	Flow (l/h)	Level (cm)	Sample Vol (l)		Silver (M)
3-Jul	7:30	150	60	5	60	125	16.9	0.02	??	125	14.8	0.02	C095	C094
3-Jul	9:30	150	60	4.8	60	125	17.8	0.02	??	125	14.7	0.02	C099	C098
3-Jul	11:30	150	60	4.8	60	125	17.4	0.02	??	125	15.2	0.02	C101	C100
3-Jul	13:30	150	60	4.7	60	125	17	0.02	??	125	15	0.02	C103	C102
3-Jul	15:30	150	60	4.8	60	125	16.8	0.02	??	125	15.2	0.02	C110	C104

Test# 7

Conditions

Date 08/07/02

Material Mixed from customer

Temperature 60 oC

Anolyte 8M HNO₃, 0.5M AgNO₃ (5l)

Catholyte 8M HNO₃ (5l)

Current 60 A

Ultrasound 150 W sweep

Duration 8 h

Start and end results

Copper oxalate in sample (start) 513.6 ma

Copper in sample (start) 203.11 mg

Copper in sample (end) 35.03 mg

Copper in solution (end) 152.29 mg

Weight of sample (start) 50.0152 a

Weight of sample (end)1* 21.96 a

Weight of sample (end)2* 12.86 a

*organics 15.1952 a

2 cemented, 1 non-cemented

Anolyte level to Volume conversion

slope 202.982

intercept 475.483

Catholyte level to Volume conversion

slope 238.529

intercept 226.349

Conclusions 69.01 in anolyte. 5.96 in catholyte. 17.25 in solids 92.22 total (DF 5.80)

Data section														
Physical parameters													Samples collected	
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte
		Watts	A	V	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)		Silver (M)
8-Jul	7:00	150	60	4.8	59	125	16	0.02	??	125	16	0.02	C117	C116
8-Jul	9:00	150	60	4.8	59	125	16.2	0.02	??	125	16.2	0.02	C119	C118
8-Jul	11:00	150	60	4.8	61	125	15.7	0.02	??	125	16.5	0.02	C123	C122
8-Jul	13:00	150	60	4.8	61	125	15.2	0.02	??	125	16.7	0.02	C127	C126
8-Jul	15:00	150	60	4.8	58	125	15.1	0.02	??	125	16.8	0.02	C131	C130

Test#	8	Copper oxalate $\text{Cu C}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	160.57 g/mole		
			39.55% Cu by weight		
Conditions		Start and end results		Anolyte level to Volume conversion	
Date	16/07/02	Copper oxalate in sample (start)	130.3 ma	slope	202.982
Material	Mixed from customer 1A	Copper in sample (start)	51.53 mg		
Temperature	60 °C	Copper in sample (end)	7 mg	intercept	475.483
Anolyte	8M HNO_3 , 0.5M AgNO_3 (5l)	Copper in solution (end)	33.41 mg		
Catholyte	8M HNO_3 (5l)	Weight of sample (start)	47.8556 g	Catholyte level to Volume conversion	
Current	60 A	Weight of sample (end)*12	24.14 g	slope	238.529
Ultrasound	150 W sweep	Tube only post extended treatment	10.5 g	intercept	226.349
Duration	8 h	1 samples wet	13.2156 g		
		2 post extended run			
		*organics			
Conclusions	57.54 in anolyte. 7.30 in catholyte. 13.58 in solids 78.43 total (DF 7.36)				

Data section															
Physical parameters													Samples collected		Analytical
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte	
		Watts	A	V	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)			Silver (M)
16-Jul	7:00	150	60	4.8	60	125	16.5	0.02 ??	125	16.8		0.02	C167	C166	0.4683
16-Jul	9:00	150	60	4.8	60	125	15.7	0.02 ??	125	16		0.02	C169	C168	0.4858
16-Jul	11:00	150	60	4.9	74	125	16.3	0.02 ??	125	15.7		0.02	C171	C170	0.4674
16-Jul	13:00	150	60	5.1	59	125	14	0.02 ??	125	17		0.02	C173	C172	0.4599
16-Jul	15:15	150	60	5.1	60	125	12	0.02 ??	125	18.2		0.02	C175	C174	0.4493

Test# 9 Copper oxalate $\text{Cu C}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ 160.57 g/mole
39.55% Cu by weight

Conditions
Date 18/07/02
Material Mixed from customer 1B
Temperature 60 °C
Anolyte 8M HNO_3 , 0.5M AgNO_3 (5l)
Catholyte 8M HNO_3 (5l)
Current 60 A
Ultrasound 150 W sweep
Duration 8 h

Start and end results
Copper oxalate in sample (start) 137 mg
Copper in sample (start) 54.18 mg
Copper in sample (end) 0.85 mg
Copper in solution (end) 53.38 mg
Weight of sample (start) 36.41 g
Weight of sample (end)* 23.87 g
metal 1 (32.4g) 30.8 g
metal 2 (~44.68g) 43.86 g
metal 3 (~44.68g) 43.15 g
*organics Δ 12.54 g

Anolyte level to Volume conversion
slope 202.982

intercept 475.483

Catholyte level to Volume conversion
slope 238.529
intercept 226.349

Conclusions 93.56 in anolyte. 4.96 in catholyte. 1.57 in solids 100.09 total (DF 63.74)

Data section														
Physical parameters													Samples collected	
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte
		Watts	A	V	Temp (°C)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (°C)	Flow (l/h)	Level (cm)	Sample Vol (l)		Silver (M)
18-Jul	7:15	150	60	4.7	61	125	17.5	0.02	??	125	16.2	0.02	C185	C184
18-Jul	9:10	150	60	4.7	61	125	17.5	0.02	??	125	16.2	0.02	C187	C186
18-Jul	11:10	150	60	4.8	61	125	17.1	0.02	??	125	16.5	0.02	C189	C188
18-Jul	13:25	150	60	4.8	62	125	16.9	0.02	??	125	16.5	0.02	C201	C200
18-Jul	15:25	150	60	4.8	62	125	16	0.02	??	125	17.4	0.02	C203	C202

Test#	10	Copper oxalate $\text{Cu C}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	160.57 g/mole	
			39.55% Cu by weight	
Conditions		Start and end results		Anolyte level to Volume conversion
Date	01/08/02	Copper oxalate in sample (start)	137 ma	slope 202.982
Material	Mixed from customer 1B chopped	Copper in sample (start)	54.18 mg	
Temperature	60 oC	Copper in sample (end)	2.94 ma	intercept 475.483
Anolyte	8M HNO_3 , 0.5M AgNO_3 (5l)	Copper in solution (end)	42.48 mg	
Catholyte	8M HNO_3 (5l)	Weight of sample (start)	46.597 g	Catholyte level to Volume conversion
Current	60 A	Weight of sample (end)1*	27.5 g	slope 238.529
Ultrasound	150 W sweep	*organics	19.097 g	intercept 226.349
Duration	8 h	1 verv wet		

Conclusions 74.23 in anolyte. 4.17 in catholyte. 5.43 in solids 83.83 total (DF 18.43)

Data section														
Physical parameters													Samples collected	
Date	Time	US Power	Current	Voltage	Anolyte				Catholyte				Anolyte	Catholyte
		Watts	A	V	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)	Temp (oC)	Flow (l/h)	Level (cm)	Sample Vol (l)		Silver (M)
1-Aug	7:30	150	60	4.7	61	125	17.5	0.02	??	125	16.5	0.02	C237	C236 0.4713
1-Aug	9:30	150	60	4.9	61	125	17.5	0.02	??	125	16.8	0.02	C239	C238 0.4365
1-Aug	11:30	150	60	4.8	61	125	17.1	0.02	??	125	15.8	0.02	C241	C240 0.4395
1-Aug	13:30	150	60	4.8	62	125	16.9	0.02	??	125	16	0.02	C243	C242 0.424
1-Aug	15:30	150	60	4.9	60	125	16	0.02	??	125	16.4	0.02	C245	C244 0.4029

Appendix 3

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