University of Alberta

Supercritical Fluid Extraction of Copper from Soil

by

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ABSTRACT

Supercritical fluid extraction (SFE) is a promising new technology that is used to remediate metal-contaminated soils. Supercritical carbon dioxide (SC CO_2) was used to extract copper from two types of spiked soil (i.e. silt and sand). Extraction experiments were carried out by using thenoyltrifluoroacetone (tta) and tributylphosphate (TBP) as chelating agents. Extraction experiments were conducted at temperatures and pressures ranging from $35^{o}C$ to $40^{o}C$ and 17.2 MPa to 24.1MPa, respectively. Of the various extractions investigated, appreciable amount of copper is extracted from sand at 24.1 MPa and $35^{o}C$. The extraction efficiency increases from 36 % to 56 % for the sand. At the same conditions of temperature and pressure, the extraction efficiency for silt is only 12%. An analysis performed on sand and silt samples indicated that several other metals are present in the silt soil and sand soils and are co-extracted with copper.

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LIST OF ACRONYMS

acac	**Acetylacetone**
CO_2	**Carbon Dioxide**
CFCs	**Chlorofluorocarbons**
EPA	**Environmental Protection Agency**
hfa	**Hexafluoroacetylacetone**
ICP-MS	**Inductively Coupled Plasma Mass Spectrometry**
PCBs	**Polychlorinated Biphenyls**
Pc	**Critical Pressure**
RODs	**Records of Decision**
SFE	**Supercritical Fluid Extraction**
SCF	**Supercritical Fluids**
SC CO_2	**Supercritical Carbon Dioxide**
S/S	**Solidification/ Stabilization**
SVOCs	**Semivolatile Organic Compounds**
tfa	**Trifluoroacetylacetone**
TBP	**Tribulyl Phosphate**
Tc	**Critical Temperature**
tta	**Thenoyltrifluoroacetone**
VOCs	**Volatile Organic Compounds**

CHAPTER 1 INTRODUCTION

1.1 PROBLEM STATEMENT

Increasing industrial development results in an increase in contaminated land, which is of growing concern around the world. There are 30,000 contaminated sites alone in Canada (Saldana *et al.*, 2005). Soil contamination results from a number of causes, including the dumping of hazardous substances, pesticide and fertilizer use, and industrial or chemical processes (U.S. EPA, 2006). The contaminants include metals, organics or radionuclides (Stiver *et al.*, 1993). Many industrial processes concentrate metals like copper, cadmium, lead and zinc. These can then end up in the earth.

Metals are of great concern at many contaminated sites and are present at most Superfund sites (U.S. EPA, 1997b). Approximately 75% of Superfund sites for which Records of Decision (RODs, which indicate what type of cleanup alternatives will be used to cleanup the site) have been signed contain metals as a form of contamination (Evanko *et al.*, 1997). Metals occur naturally in soil in small amounts, and life on Earth has evolved to cope with only small exposure to these elements. In Alberta, according to the National Pollutant Release Inventory data for 2005, approximately 16.96 tonnes of copper, 550 tonnes of zinc, 191.23 tonnes of lead and 17 tonnes of arsenic were released to the air, water and soil (EC, 2007).

Metals including lead, chromium, arsenic, zinc, cadmium, copper and mercury can cause significant damage to the environment and human health as a result of their mobilities and solubilities (Mulligan *et al.*, 2001). Their presence in ground water and soils may significantly pose a threat to the human health and ecological system (Evanko *et al.*, 1997). Metals may adsorb onto the soil, run off into rivers or lakes or leach in the groundwater, an important source of drinking water (Mulligan *et al.*, 2001). However, due to precipitation and adsorption reactions, metals are often immobile in the subsurface system. Therefore remediation activities at metals-contaminated sites have often focused on the solid phase sources of metals i.e. contaminated soils, sludges, wastes, or debris (Evanko *et al.*, 1997).

Over the past years, use of metals such as copper, cadmium and zinc have increased substantially as shown in Table 1.1.

Table 1.1: Global production of metals and the rate of metals reaching the soil (10^3 ton/year) (adapted from Mulligan *et al.*, 2001)

Metal	Global Production (10^3 ton/year)				Emission to the soil in the 1980s (10^3 ton/year)
	1975	1980	1985	1990	
Cd	15.2	18.2	19.1	20.2	22
Cu	6739.0	7204.0	7870.0	8814.0	954
Pb	3432.2	3448.2	3431.2	3367.2	796
Zn	3975.4	4030.3	7423.1	5570.9	1372

If present at sufficient concentrations, contaminants such as heavy metals and others can prevent plants from growing, leaving the soil vulnerable to erosion (Brown, 1994). Some of these substances can accumulate in plants and animals, thus moving into the human food chain (Saldana *et al.*, 2005). Metals can bioaccumulate in the following order, river sediments, bacteria, turbicids, and then fish and man (if one consumes these fish) (Mulligan *et al.*, 2001). Soil remediation is often necessary to protect the air, surface water, groundwater and living organisms. A wide variety of treatment technologies are used for remediation of metals-contaminated soil and groundwater at Superfund sites (Evanko *et al.*, 1997). These technologies can be grouped under four basic categories: thermal technologies such as incineration or vitrification; biological technologies such as biodegradation; stabilization technologies such as fixation by Portland cement; and separation based technologies where the contaminants are extracted from the environmental matrix (Akgerman, 1993). Some of these techniques are still at their developmental stages while others technologies have not been commercialized yet but are promising.

Supercritical fluid extraction (SFE) is a promising new technology that may be used to remediate metal-contaminated sites. SFE is becoming an important process, as well as a tool in analytical science, which has seen rapid development over the last few years. SFE has the potential to quickly and effectively remove the contaminants from soil, allowing for site redevelopment (Stiver *et al.*, 1993).

Supercritical fluids (SCFs) have gained much attention as an environmentally friendly alternative to organic solvents commonly used in the chemical manufacturing processes. A SCF is simply a substance above its critical point defined by the critical pressure (Pc) and critical temperature (Tc), which is the highest temperature and pressure at which its vapour/ liquid equilibrium exists (Brennecke, 1996). The pressure/ temperature region of existence of a SCF is illustrated in Figure 1.1. At liquid like densities, SCF exhibit a gas like viscosity and high diffusion rate (Koga *et al.,* 2005).

These qualities make SCF effective and selective solvents. These properties result in several advantages in extraction such as easy solvent recovery by simple depressurization, elimination of residual solvent in the extracted medium, lower pressure drops, and higher mass transfer rates (Akgerman, 1993).

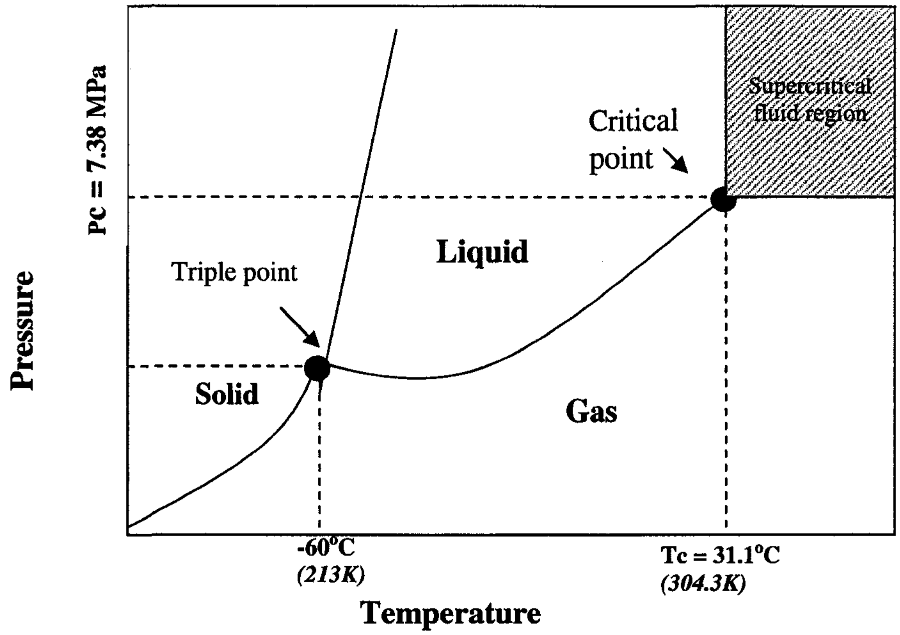


Figure 1.1: Pressure-Temperature phase diagram for carbon dioxide (CO_2) (adapted from Saldana *et al.*, 2005)

The most commonly used supercritical solvent is supercritical carbon dioxide (SC CO_2). CO_2 is non-flammable, non-toxic, non-reactive and has a moderate critical point of 31°C and 7.38 MPa, is available at low cost and is easily recycled (Wang *et al.*, 2001). Pure SC CO_2 is non-polar and is a good solvent for hydrocarbons and non-polar compounds (Laitinen *et al.*, 1994). The addition of modifiers like water and methanol can increase the polarity of supercritical SC CO_2 (Lui *et al.*, 2002), which increases its ability to solubilize slightly polar species.

1.2 RESEARCH OBJECTIVES

There are many treatment technologies used for the remediation of contaminated environmental matrices. Among them supercritical fluid extraction (SFE) is becoming a popular technique for the extraction and recovery of a wide range of organometallic and inorganic analytes from samples (Burford *et al.*, 1999). Supercritical fluid extraction of metals is challenging, but still promising.

Supercritical carbon dioxide has been used extensively for the extraction of metals from the soil. However little information is available in the literature regarding supercritical fluid extraction (SFE) of metal species. Heavy metals like Cd, Cu, As, Cr, Fe, and Zn can be effectively removed from solid matrices by SC CO_2. For SFE of these heavy metals different chelating agents have been used. It is generally known that β-diketones such as thenoyltrifluoroacetone (tta) are useful chelating agents for supercritical fluid extraction (SFE) of various metal ions. The previous work was done on the extraction of Cu metal from soil using thenoyltrifluoroacetone (tta) as chelating agent. Experiments were carried out at conditions of 10.34 MPa pressure and 40°C temperature.

The research herein focuses on the use of laboratory scale SFE system to investigate the extraction of copper from soil. Copper was chosen for the SFE, because it is a heavy metal which is safe and easy to handle and extract from the soil matrix.

The main objective of this research work is therefore to extract copper from artificially contaminated soil. In particular, the objectives were to:

- modify the SFE experimental setup and to develop methods to allow the study of copper extraction from soil using SFE.
- determine the extraction efficiency of copper from an artificially contaminated sand and silt using a mixture of thenoyltrifluoroacetone (tta) and tributylphosphate (TBP) as the chelating agent.

The background information and issues related to the SFE of metals are presented in Chapter 2. Chapter 2 also provides a review of the current technologies used for the treatment of soil contaminated by organics and metals with a description of SFE as soil remediation technology. Chapter 3 provides details of the methodology used for the extraction of copper from soils, including experimental methods and sample analysis. Chapter 4 provides the results and discussion. Conclusions and recommendations are presented in Chapter 5.

CHAPTER 2 LITERATURE REVIEW

Remediation of contaminated soil is a challenge due to the diverse nature of the compounds that contaminate soil and the complexity of the soil matrix (Stiver *et al.*, 1993). Successful remediation of soil contamination should not be defined as returning the site to pristine conditions, but rather reducing the public health risk associated with the contamination (Canter, 1990). Metal contamination is a persistent problem at many contaminated sites (Evanko *et al.*, 1997). Cadmium, copper, lead, mercury, nickel and zinc are considered the most hazardous heavy metals and are included on the US Environmental Protection Agency's (EPA) list of priority pollutants (Cameron, 1992). A range of technologies are available for remediation of metal-contaminated soil and ground water at Superfund sites (Evanko *et al.*, 1997) and some of these will be discussed in the following Sections.

2.1 SOIL REMEDIATION TECHNOLOGIES

The primary aim of remediation is to reduce the actual environmental threat and the potential risk, so that unacceptable risks are reduced to acceptable levels. In general, remediation technologies can be grouped into categories of physical, chemical, and/or biological processes (United Nations, 2000).

Treatment technologies can be applied *in-situ* or *ex-situ*. *Ex-situ* refers to processes applied to excavated soil either on-site or off-site. *In-situ* refers to processes occurring in unexcavated soil, which remains relatively undisturbed. These two categories are then further divided into technologies according to the mechanism employed; chemical, physical or biological and their application for organic or inorganic contaminations (United Nations, 2000). Different soil remediation technologies are listed in Table 2.1. Each approach has specific advantages and disadvantages, and many of the methods are still in the developmental stages and may not yet be available commercially. These technologies are discussed further, beginning with *in-situ* technologies and following with *ex-situ* technologies and are briefly summarized in Table 2.1.

2.1.1 *In-situ* biological processes

The objective of biological remediation processes is the degradation of contaminants to harmless intermediates and end products (Wood, 1997). These technologies are commonly used for the remediation of organic contaminants and are beginning to be applied for metal remediation, although most applications (for metal remediation) to date have been at the bench-and pilot-scale.

Bioremediation

In these processes, microorganisms are stimulated to grow and use the contaminants as a food or energy source by providing favorable environment and conditions (temperature, nutrients, etc.). Residual treatment is not required after the degradation of the contaminants. Biological processes are least cost effective; require more time and do not always lead to complete destruction of the contaminants (Van Deuren *et al.,* 2002).

Table 2.1: **Summary of commonly used soil remediation technologies:**

	IN- SITU		*EX-SITU*	
MECHANISM	**ORGANIC CONTAMINANTS**	**INORGANIC CONTAMINANTS**	**ORGANIC CONTAMINANTS**	**INORGANIC CONTAMINANTS**
PHYSICAL	1. Soil vapour extraction 2. Containment system/ Reactive Walls/ Barriers	1. Containment 2. Electrokinetics	1. Incineration 2. Thermal desorption 3. Soil vapour extraction 4. Mechanical separation 5. Excavation & disposal	1. Excavation & disposal
CHEMICAL	1. Soil washing 2. Stabilization/ Solidification	1. Soil washing 2. Stabilization/ Solidification	1. Soil washing 2. Stabilization/ Solidification 3. Dehalogenation 4. Solvent extraction	1. Soil washing 2. Stabilization/ Solidification 3. Solvent extraction 4. Chemical reduction and oxidation
BIOLOGICAL	1. Bioremediation 2. Phytoremediation 3. Natural attenuation 4. Vitrification	1. Vitrification 2. Phytoremediation	1. Land farming 2. Bioreactors 3. Vitrification	1. Vitrification

Biodegradation is the decomposition of chemicals into sub-units and is therefore mostly applicable to organic contaminants. In some cases organic contaminants are coincidentally biodegraded as a result of microbial activity on other carbon compounds in a process called co-metabolism. Some compounds are broken down into more potentially toxic by-products during the bioremediation process, for example TCE to vinyl chloride (United Nations, 2000). For *in-situ* applications, these by-products may be mobilized to ground water or contacted directly if no control techniques are used (Van Deuren *et al.*, 2002). All organic compounds are not amenable to biodegradation. Bioremediation techniques are used to remediate soils, sludges, and ground water contaminated by petroleum hydrocarbons, solvents, pesticides, wood preservatives, and other organic chemicals (Van Deuren *et al.,* 2002). Bioremediation can be used to change the valence state of inorganics and cause adsorption, immobilization onto soil particulates, precipitation, uptake, accumulation, and concentration of inorganics in micro or macroorganisms (Van Deuren *et al.,* 2002). These techniques are still in the experimental stages, but show considerable promise of stabilizing or removing inorganics from soil. There are some examples of research done on the bioremediation of soil contaminated with heavy metals. For example microbially catalyzed reactions have been integrated in a microbiological process to remove toxic metals from contaminated soil (White *et al.*, 1998). A bacterium called *Alcaligenes eutrophus CH34* was used to remediate heavy metal contaminated soil by either solubilizing the metals or increasing their bioavailability (Diels *et al.,* 1999). Gray (1998) used fungi called *Mycelium* as a bioremediation agent to treat soil contaminated with heavy and radioactive metals.

Phytoremediation

Phytoremediation may be applicable for the remediation of metals, pesticides, solvents, explosives, crude oil, PAHs, and landfill leachates (Van Deuren *et al.,* 2002). In this process, plants are used to remove, transfer, stabilize, and destroy contaminants in soil and sediment (Van Deuren *et al.,* 2002). Hyperaccumulator plants, capable of mobilizing and recovering metals, are grown on the contaminated area and then harvested to remove the metals from the site (Wood, 1997). Plants may metabolize certain organics, or transport them above ground where they are transpired or chemically altered, but metals can be accumulated in the roots or above ground (United Nations, 2000). The use of plants to remediate metal-contaminated soil may take as long as a decade, however the projected cost of this process is far less than the more traditional excavation and landfilling methods (Brown, 1994). Potentially useful phytoremediation technologies for remediation of metals-contaminated sites include phytoextraction and phytostabilization (U.S. EPA, 1996b). Phytoextraction employs hyperaccumulating plants to remove metals from the soil by absorption into the roots and shoots of the plant (Evanko *et al.*, 1997). Phytostabilization involves the use of plants to limit the mobility and bioavailability of metals in soil (Evanko *et al.*, 1997).

2.1.2 *In-situ* physical processes

Physical processes separate contaminants from uncontaminated material by exploiting differences in their physical properties (e.g. density, particle size, volatility) by applying some external forces (e.g. abrasion) or by altering some physical characteristics to enable separation to occur (e.g. flotation) (Wood, 1997). *In-situ* physical processes are further categorized into electrokinetic separation, thermal treatment, containment system and soil vapor extraction.

Electrokinetic separation

The electrokinetic remediation (ER) process removes metals and organic contaminants from low permeability soil, mud, sludge, and marine dredging (Van Deuren *et al.,* 2002). Electrokinetic remediation technologies apply a low density current to the contaminated soil in order to mobilize contaminants in the form of charged species (Evanko *et al.*, 1997). This current mobilizes charged species, causing ions and water to move toward the electrodes. Electrokinetic treatment concentrates contaminants in the solution around the electrodes. The current produces an acid front at the anode and a base front at the cathode (Evanko *et al.*, 1997). The contaminants are removed from the soil by a variety of processes, including electroplating at the electrodes, precipitation/ co-precipitation at the electrodes, complexation with ion exchange resins, or by removing water from the subsurface and treating it to recover the extracted metals (Smith *et al.*, 1995). The electrokinetic process can potentially remove high levels of metal contaminants *in-situ,* and this treatment method is the only method which can currently do this (United Nations, 2000). The electrokinetic remediation method depends strongly on mineralogical composition of the soil as well as on soil organic matter content (Reddy *et al.,* 2005). The efficiency of metal removal by this process will be influenced by the type and concentration of contaminant, the type of soil, soil structure and interfacial chemistry of the soil (Evanko *et al.*, 1997). The use of solubilizing/complexing agents, such as chelating agents and other extractants, is one of the possible approaches to enhance the efficiency of removing these metals from the soils (Reddy *et al.* 2005).

In-situ thermal treatments

Thermal treatment offers quick cleanup times, but it is generally the most costly treatment technology group. The process is similar to standard soil vapor extraction (SVE), in which vacuum is applied to the soil, but thermal treatment requires heating of the soil and thus the installation of heat resistant extraction wells. Thermally enhanced soil vapor extraction (SVE) is an extraction technique that adds a heat source, either via hot air or stream injection, or electric/radio-frequency heating, to volatize organic contaminants and aid in their removal (United Nations, 2000). Thermally enhanced SVE may require off-gas and/or residual liquid treatment. This process can fail to achieve the desired level of decontamination due to substrate heterogeneity (United Nations, 2000). This technology can treat some pesticides, volatile organics or fuels but cannot be used for metal removal. In situ SVE will not remove heavy oils, metals, PCBs, or dioxins, because the process involves the continuous flow of air through the soil, however, it often promotes the *in-situ* biodegradation of low-volatility organic compounds that may be present (Van Deuren *et al.*, 2002)..

Containment

Containment is necessary whenever contaminated materials are to be buried or left in place at a site. In general, containment is performed when extensive subsurface contamination at a site precludes excavation and removal of wastes because of potential hazards, unrealistic cost, or lack of adequate treatment technologies (Van Deuren *et al.*, 2002). The concept of containment as a method for dealing with contaminated soil is based on the use of low permeability barriers to isolate the contaminated material, or any associated leachate or gaseous products, from the environment (Wood, 1997). The barriers can be made from natural or synthetic materials, which can be placed under, over or around the contaminated site. This method does not remediate the site: it only prevents the spread of the contaminants. A common containment wall consists of a mixture of bentonite and soil; bentonite is an absorbent which allows the contaminated water to pass but which collects the contaminants via surface absorption (United Nations, 2000). Containment treatments offer quick installation times and are typically a low to moderate cost treatment group (Van Deuren *et al.,* 2002). This process can be used to remediate all organic and inorganic contaminated soil including heavy metal contaminated soil.

2.1.3 *In-situ* Chemical processes

Chemical treatment processes for the remediation of contaminated soil are designed either to destroy contaminants or to convert them to less environmentally hazardous forms (Wood, 1997).

Solidification/stabilization

Solidification/stabilization (S/S) methods operate by solidifying contaminated material, converting them into a less mobile chemical form and/or by binding them within an insoluble matrix offering low leaching characteristics (Wood, 1997). Unlike other remedial technologies, (S/S) seeks to trap or immobilize contaminants within their "host" medium (i.e., the soil, sand, and/or building materials that contain them) instead of removing them through chemical or physical treatment (Van Deuren *et al.,* 2002). In stabilization processes, the chemical reactions that occur yield less mobile compounds containing the contaminant or bind the contaminant to the substrate. This is a quick and inexpensive way to prevent the contaminants from spreading, however an eventual clean up of the site will be more difficult.

The target contaminant group for *in-situ* (S/S) is generally inorganics (including radionuclides). Treatment of organic contaminants is generally more difficult and more expensive (Wood, 1997).

Soil flushing

In-situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions that may contain required additives (Van Deuren *et al.,* 2002). An aqueous extracting solution is injected into or sprayed onto the contaminated area to mobilize the contaminants usually by solubilization (Evanko *et al.,* 1997). The contaminated water is then recovered and brought to the surface for treatment as needed. Soil flushing is an inadequate treatment because of subsurface channeling and the possible need for post treatment of the soil to remove the additives (United Nations, 2000). This process is used to treat halogenated and non-halogenated volatile organics, inorganics and radionuclides.

2.1.4 *Ex-situ* biological processes

The main advantage of *ex-situ* treatment is that it generally requires shorter time periods than *in-situ* treatment, and there is more certainty about the uniformity of treatment because of the ability to homogenize, screen, and continuously mix the soil. However, *ex-situ* treatment requires excavation of soils, leading to increased costs. *Ex-situ* biological processes include landfarming and slurry phase bioreactors.

Bioreactors or Slurry-phase biodegradation

Bioreactors vary considerably in their operating conditions, but the principal emphasis is in stimulating the biological degradation rate by choosing the optimum temperature, pollutant concentration, degree of aeration and other factors (United Nations, 2000). In bioreactors, pretreated soils are slurried with water and treated in a custom built reactor system with a mechanical agitation device (Martin *et al.,* 1996). The slurry is kept at controlled operating conditions and oxygen and nutrients are continuously supplied until the remediation is complete (United Nations, 2000). When biodegradation is complete, the soil slurry is dewatered. Dewatering devices that may be used include clarifiers, pressure filters, vacuum filters, sand drying beds, or centrifuges (Van Deuren *et al.,* 2002). This technique is used to treat halogenated VOCs and SVOCs, pesticides, and PCBs in excavated soils and dredged sediments. Bioreactors are ineffective for heavy metal contaminated soils.

2.1.5 *Ex-situ* physical/chemical treatment

Physical/chemical treatment uses the physical properties of the contaminants to destroy (i.e., chemically convert), separate, or immobilize the contamination. Chemical reduction/oxidation and dehalogenation are destruction technologies. Soil washing, soil vapor extraction (SVE), and solvent extraction are separation technologies, while Solidification/Stabilization (S/S) is an immobilization technology. *Ex-situ* physical/chemical treatments are categorized into chemical extraction, chemical oxidation/reduction, dehalogenation, separation, soil washing and solidification/stabilization.

Solvent extraction

Solvent extraction is a common form of chemical extraction that uses an organic solvent as the extractant. When the contaminants are transferred to the solvent, the contaminant-laden solvent is then treated to remove the pollutant so that the solvent may be reused. Traces of solvent may remain within the treated soil matrix, so the toxicity of the solvent is an important consideration (Van Deuren *et al.,* 2002). This technology can be applied successfully to some volatile organics (halogenated or non-halogenated) and fuels, and can remove organically-bound heavy metals i.e. heavy metals that are bonded with carbon (United Nations, 2000). Organically bound metals can be extracted along with the target organic contaminants, thereby creating residuals with special handling requirements.

Common extractants used in solvent extraction include acids. Acid extraction uses hydrochloric acid to extract heavy metal contaminants from soils. In this process, soils are first screened to remove coarse solids. Hydrochloric acid is then introduced into the soil in the extraction unit. The soil-extractant mixture is continuously pumped out of the mixing tank, and the soil and extractant are separated using hydrocyclones (Van Deuren *et al.,* 2002). When extraction is complete, the soils are rinsed with water to remove entrained acid and metals. Finally, the soils are dewatered and mixed with lime and fertilizer to neutralize any residual acid (Van Deuren *et al.,* 2002).

Chemical oxidation/reduction

Reduction/oxidation (Redox) reactions chemically convert hazardous contaminants to less toxic compounds that are more stable and less mobile. Redox reactions can be applied to soil remediation to achieve a reduction of the toxicity or a reduction of the solubility of the contaminants (Wood, 1997). A redox reaction is a chemical reaction, in which electrons are transferred from one compound to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). The oxidizing agents that can be used for treatment of contaminants are oxygen, ozone, hydrogen peroxide, hypochlorites, chlorine, chlorine dioxide, and ultraviolet light (United Nations, 2000). Changing the oxidation state of metals by oxidation or reduction can detoxify, precipitate, or solubilize metals (Evanko *et al.,* 1997). The target contaminant group for chemical redox is inorganics. The technology can be used but may be less effective against nonhalogenated VOCs and SVOCs, fuel hydrocarbons, and pesticides (Van Deuren *et al.,* 2002).

Separation

Separation processes are used to remove contaminated concentrates from soils. *Ex-situ* separation can be performed by many processes. Several techniques are available for physical separation of contaminated soil including screening, classification, gravity concentration, magnetic separation and froth flotation (Evanko *et al.,* 1997). Magnetic separation, on the other hand, is a much newer separation process that is still being tested (Evanko *et al.,* 1997).The target contaminant groups for *ex-situ* separation processes are SVOCs, fuels, and inorganics (including radionuclides). The technologies can be used on selected VOCs and pesticides. Magnetic separation is specifically used on heavy metals, radionuclides, and magnetic radioactive particles, such as uranium and plutonium compounds (Van Deuren *et al.,* 2002). Magnetic separation subjects particles to a strong magnetic field using electromagnets and relies on differences in magnetic properties of the minerals for separation (Evanko *et al.,* 1997).

Soil washing

Soil washing systems incorporating most of the technologies previously described offer the greatest promise for application to soils contaminated with a wide variety of heavy metal, radionuclides, and organic contaminants (Van Deuren *et al.,* 2002). Commercial soil washing systems are still not yet widely available. Contaminants which are sorbed onto soil are separated from soil in an aqueous-based system (United Nations, 2000). The wash water may also be augmented with an acidic or basic leaching agent, surfactant, or chelating agent to help remove organics or heavy metals (United Nations, 2000). These agents help desorb the contaminants, but they are costly and wash water needs some treatment prior to the disposal (United Nations, 2000).

Stabilization/Solidification

In e*x-situ* stabilization/solidification (s/s), contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization) (Van Deuren *et al.,* 2002). In *ex-situ* S/S, the resultant material requires disposal. Stabilization/solidification is a relatively inexpensive method for treating soils contaminated with inorganics, including radionuclides (United Nations, 2000).

2.1.6 *Ex-Situ* thermal processes

Thermal processes use heat to increase the volatility (separation) of contaminants or to burn, decompose, or detonate (destruction); or melt (immobilization) the contaminants (Van Deuren *et al.,* 2002). Three *ex-situ* techniques are thermal desorption, incineration and vitrification. Thermal treatments offer quick cleanup times but are typically the most costly treatment group.

Thermal desorption

In thermal desorption, the water and contaminants in hazardous waste are volatilized by heating the waste to moderately high temperatures, ranging from 100° to 550°C (United Nations, 2000). At these temperatures, the volatile contaminants are evaporated and subsequently removed from the exhaust gases by condensation, scrubbing, filtration or destruction at higher temperatures (Wood, 1997). Thermal desorption is a physical separation process and is not designed to destroy contaminants; wastes are heated sufficiently to volatilize water and organic contaminants. A carrier gas or vacuum system transports volatilized water and organics to a gas treatment system. The bed temperatures and residence times designed into these systems will volatilize selected contaminants but will typically not oxidize them (Van Deuren *et al.,* 2002). This process has also been used for the treatment of mercury-contaminated soils (Wood, 1997).

Incineration

Incineration involves the heating (either directly or indirectly) of excavated soil to temperatures ranging from 880 to 1200°C to destroy or detoxify contaminants (Wood, 1997). Incineration is also used to treat contaminated liquid and sludges. One disadvantage of incineration is that it destroys soil texture and removes all natural humic components. Exhaust gases are also treated in order to remove particulates and other combustion products (Wood, 1997). Four common incinerator types are rotary kiln, liquid injection, fluidized bed and infrared (United Nations, 2000). Incineration is used to remediate soils contaminated with explosives and hazardous wastes, particularly chlorinated hydrocarbons, PCBs, and dioxins (Van Deuren *et al.,* 2002). Metals cannot be treated by incineration, because they may react with chlorine in the waste to form more volatile or potentially toxic compounds than the original pollutants (United Nations, 2000).

Vitrification

Vitrification involves the heating of excavated soil to temperatures in the region of 1000 to 1700°C that will cause soil to melt and form a glass when cooled (Wood, 1997). The high temperatures destroy any organic constituents with very few byproducts and immobilize inorganics by trapping them in the glassy matrix. Vitrification may be best suited for difficult to treat wastes such as mixtures of organics and metals (U.S. EPA, 1997b). Materials, such as heavy metals and radionuclides, are actually incorporated into the glass structure, which is strong and durable and is resistant to leaching.

Other treatment technologies for soil are excavation and disposal, in which contaminated material is removed and transported to permitted off-site treatment and/or disposal facilities (Van Deuren *et al.,* 2002). Some pretreatment of the contaminated media usually is required in order to meet land disposal restrictions.

2.2 NON COMMERCIAL SOIL REMEDIATION TECHNIQUES

There are several new techniques, which have not been commercialized yet but are very promising. Some of these techniques are presented in the following sections.

2.2.1 Polymer adsorption

Water-soluble polymers with functional groups having a strong affinity for heavy metals are used to clean up contaminated soils (United Nations, 2000). The metals are stripped from and attached to the polymer, when a polymer solution is passed through the soil. The polymer is designed in a way, so that it will not be absorbed to the soil and can be treated in *ex-situ* to release the metals. The metal is recovered and the polymer is recycled. This process can remove toxic heavy metals such as Pb, Cr and Cd more effectively (United Nations, 2000).

2.2.2 Plasma arc (*Ex-situ)*

This technique utilizes high temperature (10,000°C or even higher) pyrolysis, which results from the discharge of a large electric current in an inert gas, to convert hazardous chemicals such as PCBs, pesticides, CFCs and halogen gases into innocuous and safe emitted products (United Nations, 2000). The hazardous substances first break down into their atomic constituents within the plasma and then they are converted into harmless substances. This technology is used to safely destroy PCBs, dioxins, furans and pesticides.

2.2.3 Solar detoxification (phytolysis) (*Ex-situ*)

This is an emerging remedial technology for the destruction of a wide range of hazardous organic chemicals in soil and/or water by photocatalytic oxidation or direct thermal decomposition (United Nations, 2000). Vacuum extraction is used to first remove the contaminants from the soil, vacuum extraction is then followed by condensation, in which they are mixed with a semiconductor catalyst (titanium oxide) and passed through a reactor illuminated by sunlight or exposed to UV radiation from electric lamps. The light activates the catalyst to generate a reactive species known as hydroxyl radicals, which are powerful oxidizers that can decompose the contaminants into non-toxic by products like water, CO_2 and inorganic salts. This process can remove pesticides, explosives, VOCs, SVOCs, solvents, heavy metals, PCBs, furans, dioxins and other contaminants.

2.2.4 Lasagna^{TM} process

The Lasagna^{TM} process is an *in-situ* remediation technology developed by an industrial consortium to remediate soil contaminated with soluble organic compounds. This technology uses electro-osmosis, biodegradation and physiochemical treatment processes to treat soil and electrokinetics to move contaminants in soil pore water into treatment zones. When the electrodes are energized by direct current, the soil is warmed up and the water and soluble contaminants move into or through the treatment layers. In the treatment layers that contain reagents, the soluble organic contaminants are decomposed or immobilized (United Nations, 2000). The immobilized contaminants can then be removed and disposed of. The water that accumulates at the cathode can be recycled back to the anode for acid-base neutralization.

2.3 SUPERCRITICAL FLUID EXTRACTION

Supercritical fluid extraction is a novel technique for the remediation of contaminated soil (Stiver *et al.,* 1993). Minimizing liquid waste generation, easy separation of solutes and fast reaction rates are some of the advantages of SFE technology over conventional solvent extraction methods (Gopalan *et al.,* 2003). In comparison to conventional solvent extraction, SFE allows the contaminant to be separated from the solvent (i.e. the supercritical fluid) in a concentrated form by a simple change in temperature or pressure (Saldana *et al.,* 2005). Solvent processes may require more time to remediate soil compared to SFE because of poor mass transfer of conventional solvent extraction over supercritical fluid extraction (Phelps *et al.,* 1996).

Supercritical fluid extraction is a technique in which a substance in its critical state solubilizes compounds and removes them from a matrix such as soil. This process has been used both on a commercial scale as well as on an analytical scale. This technique resembles Soxhlet extraction except that the solvent used is a supercritical fluid, a substance above its critical temperature and pressure. The basic idea of the process is to exploit the properties of supercritical solvent by contacting a contaminated matrix, which is either in a solid or liquid state with a supercritical fluid such as carbon dioxide, ethylene, water or others. The contaminant dissolve into the supercritical fluid and the mixture is extracted. The density of the extracted mixture (contaminant/ supercritical fluid) is then reduced, by either pressure reduction or heating, causing the solvent and extract(s) (i.e. the contaminant(s)) to phase separate (Baker *et al.,* 1983).

The main advantage of using supercritical fluid for extractions is that supercritical fluids extract the analytes faster and in a more environmentally friendly manner than organic solvents. Interest in supercritical fluids, particularly carbon dioxide as a solvent for use in extraction processes; have been driven by increased environmental legislation restricting the use of conventional organic solvents (Phelps *et al.,* 1996).

The following mechanism may be involved when extracting a soluble species (i.e. solutes or contaminant) from solid matrices (i.e. soil):

1. If there are no interactions between the solute and the solid phase, the process is a simple dissolution of the solute in a suitable solvent that does not dissolve the solid matrix.
2. If there are interactions between the solid and the solute, then the extraction process is termed as desorption.
3. Another mechanism is the swelling of the solid phase by the solvent accompanied by the extraction of the entrapped solute through the first two described mechanisms.
4. The fourth mechanism is reactive extraction where the insoluble solute reacts with the solvent and the reaction products are soluble and extractable.

Supercritical fluid extraction of a contaminated soil has been investigated on a bench scale as a batch process. In the batch extraction process, the pressurized supercritical fluid is introduced into the extraction vessel. The extraction vessel is equipped with temperature controllers and pressure valve at both ends. Its pressure and temperature are chosen so as to dissolve as much of the desired compound as possible. The extraction vessel is pressurized with the fluid by means of pumps, which is also necessary for the circulation of the fluid in the system. From the vessel, the fluid and the solubilized components are transferred to the separator, where the solvation power of the fluid is decreased by increasing the temperature, or more likely, decreasing the pressure of the system (Sihvonen *et al.,* 1999). The solvent expands and releases the solute, which collects at the bottom of the receptacles, while the gas is released from the top, repressurized and recirculated (Levelt Sengers, 2000).

The most commonly used supercritical solvent is supercritical carbon dioxide (SC CO_2), which is non-flammable, non-toxic, non-reactive and has moderate critical point of 31°C and 7.38 MPa, is available at low cost and is easily recycled (Lui *et al.,* 2001). Pure SC CO_2 is non-polar and is a good solvent for hydrocarbons and non-polar compounds (Laitinen *et al.,* 1994). For the extraction of more polar compounds, the polarity of SC CO_2 can be increased by adding modifiers such as methanol and water, which in turn increases the solubility of more polar compounds in the SCF and increases the ability of the SCF to displace contaminants from the soil (Bowadt and Hawthorne, 1995). Supercritical carbon dioxide has been used extensively for the extraction of metals from the soil. Direct extraction of metal ions by SC CO_2 is not efficient because of the charge neutralization requirement and weak solute-solvent interactions (Lui *et al.,* 2001). However, if metal ions are bound to organic ligands, their solubility in SC CO_2 may be significantly increased and therefore, a chelating agent is added to form a relatively non-polar metal complex (Laintz *et al.,* 1992).

Advantages of SFE

SFE is a solvent extraction technology that uses a SCF as a solvent. SFE has advantages over the conventional solvent extraction techniques due to rapid diffusion of the analytes in the fluid (gas like diffusion) and the fluid solvation power (liquid like solvation). The most significant advantages of the SFE technique are summarized as follows:

- Supercritical fluids possess higher diffusion coefficients and lower viscosities than a liquid solvent. Due to higher solubility and diffusivity in such fluids than in liquids, resulting in comparatively fast reaction kinetics (Mira *et al.*, 1999).
- In SFE, the solvation power of the fluid can be manipulated by changing pressure *(P)* and/or temperature *(T)*; therefore, it may achieve a remarkably high selectivity (Zougagh *et al.*, 2004). The property, like the tunable solvation power of supercritical fluids can also be used to extract complex samples easily.

In addition, SFE will not produce toxic by-products or residues as it simply removes the contaminant from the contaminated soil and leaves only the extract to be disposed of (Saldana *et al.*, 2005). All candidate SCFs are generally cheap, simple and many are safe. Disposal costs of the extract are much less and in large scale processes such as soil remediation, the supercritical fluids can be recycled.

Supercritical fluid extraction of contaminants from soil and sediment is a promising technique for solid waste clean up for remediation (Aria *et al.*, 2002). The extraction of contaminants from soil depends on the characteristics of soil. A new and exciting environmental application of CO_2 in the area of remediation is the extraction of metals from solutions, soil and other solid matrices (Brennecke, 1996). Supercritical CO_2 is used to extract metals from a variety of matrices by adding a suitable chelating agent. This application will be discussed further in the following section.

2.4 SUPERCRITICAL FLUID EXTRACTION OF METALS

The supercritical fluid extraction (SFE) of metal ions was assessed in terms of the ability of the process to extract, solvate, transport and collect metal species (Burford *et al.*, 1999). Supercritical fluid extraction is a technique in which a substance in its critical state solubilizes compounds and removes them from a matrix such as soil. By operating in the critical region, the pressure and temperature can be used to regulate density, which in turn regulates the solvent power of the supercritical fluid (McHugh *et al.*, 1994). The low viscosities of SCFs and high diffusivities of solutes in SCFs combined with very high buoyant forces (which cause significant density gradients across the interface) may result in superior mass transfer characteristics compared to conventional solvents (Erkey, 2000).

Carbon dioxide is a gas of choice for SFE because of its moderate critical constants ($T_c = 31°C$ and $P_c = 7.38$ MPa), inertness, and availability in pure form (Wai, 1996). Pure supercritical CO_2 is non-polar and is a good solvent for hydrocarbons and non-polar compounds (Laitinen *et al.*, 1994). However to increase the solubility of non-polar compounds in SC CO_2, a polar co-solvent, or modifier, can be added to the CO_2 (Levy *et al.*, 1992).

Direct extraction of metal ions by SC CO_2 is highly inefficient because of the charge neutralization requirement and the weak solute-solvent interactions (Wai, 1995; Yang and Mathews, 2001). However, when metal ions are chelated with organic ligands, they may become soluble in SC CO_2 (Gopalan *et al.*, 2003). SCFs modified by the addition of ligands have been utilized in the extraction of metal ions from various solid and liquid matrices (Wang *et al.*, 1995; Wang and Marshall, 1994; Johanson, 1995). These processes are illustrated in Figure 2.1.

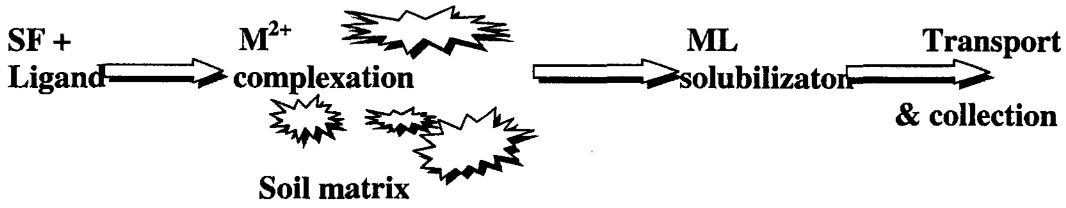


Figure 2.1: Processes involved in SFE of metals from solid matrix (adapted from Gopalan *et al,*. 2003)

Metals (such as Cu, Cr, Co, Cd, Zn, Ni, Pb and Hg for example), lanthanides and actinides have been complexed by a variety of chelating agents, including β-diketones, dithiocarbamates, organophosphorous reagents, macrocyclic ligands and crown ethers (Saldana *et al.,* 2005). Others (Lui *et al.*, 2001) have used non-ionic surfactants to form reverse micelles that can then be extracted by the SCFs.

The SFE of metals can be affected by the following parameters: solubility and stability of chelating agents, solubility of metal chelates, water content, pH, temperature and pressure of the SCF, chemical form of metal species in the solid matrix, and the nature of the solid matrix (i.e. soil type) (Gopalan *et al.*, 2003; Wai and Waller, 2000). These parameters will be discussed in the following sections.

2.4.1 Solubility and stability of chelating agents in supercritical CO_2

Solubility can be defined as the measure of how many moles of a solute (i.e. contaminant) will dissolve in one mole of SCF at a given temperature and pressure (Gupta *et al.*, 2007). If the solute of interest is not soluble in a particular supercritical solvent or solvent/co-solvent mixture, then the extraction process is not technically feasible. The solubility of chelating agent depends on its chemical nature and is different from one chelating agent to another. Some characteristics that chelating agents should possess are (Ozel *et al.,* 1999): (i) reasonable solubility in SC CO_2, (ii) formation of stable and extractable chelates with metal ions and (iii) for larger scale applications, be commercially available and inexpensive. Some chelating agents that are most commonly used for SFE of metal species are given below.

Dithiocarbamates:

Dithiocarbamate chelating agents used in the metal extractions are usually introduced as alkali metals or ammonium salts. The solubility of sodium diethyldithiocarbamate (NaDDC) in SC CO_2 is approximately 1.58×10^{-4} M (mol/L) at 50°C and 10.13 MPa compared to the solubility of 4.7×10^{-4} M for sodium bis(trifluoroethyl) dithiocarbamate (NaFDDC) at the same conditions (Wai and Wang 1997). This means that the solubility of free ligand is greatly enhanced by fluorination. Alkylammonium salts of dithiocarbamate reagents have high solubilities in SC CO_2.

One problem of using dithiocarbamates reagents is their instability in water especially in acidic solutions (Wai, 1991). When SC CO_2 is in contact with water, the water becomes acidic due to the formation and dissociation of carbonic acid and its pH at equilibrium is less than 3 (Ozel *et al.*, 2000). Dithiocarbamates will therefore break down at this pH and, to compensate, an excess amount of dithiocarbamates reagent is required to ensure high metal extraction efficiency in SFE (Wai and Wang, 1997).

β-diketones:

Successful supercritical fluid extraction (SFE) of metal compounds in the presence of complexing extractants has been carried out from solutions, spiked samples, and soil, by using β-diketones (Kersch *et al.,* 2005). β-diketones react with metal ions to form neutral chelates through the enolate anions (Wai and Wang, 1997). Acetylacetone (acac), trifluoroacetylacetone (tfa), hexafluoroacetylacetone (hfa) and thenoyltrifluoroacetone (tta) are the most common β-diketones. Of these ligands, only tta is solid at room temperature, the others being liquids at room temperature (Smart *et al.*, 1997). Little information is available on the solubility of β-diketones in SC CO_2. Solubility of acac is 4×10^{-4} mole fraction at 600°C and 13.2 MPa, while the solubility of tta is 2.3×10^{-2} mole fraction (Wai and Wang, 1997). Under supercritical fluid extraction conditions, all β-diketones show high miscibility with CO_2 (Smart *et al.*, 1997). The fluorinated β-diketones (hfa and tta) are exclusively in the enol form under high temperature and pressure conditions relevant to SFE (Wai and Wang, 1997). Free β-diketones are assumed to be stable in CO_2 under normal SFE conditions (Wai and Wang, 1997).

Organophosphorus reagents:

Organophosphorus reagents such as tributylphosphate (TBP) and phosphine oxides such as tributylphosphine oxide (TBPO), trioctylphosphine oxide (TOPO) and triphenylphosphine oxide (TPPO) have been used as ligands for extraction of actinide elements (Katz *et al.*, 1986). Most are commercially available and widely used for metal extraction in conventional solvent extraction processes (Wai and Wang, 1997). In particular, tributylphosphate (TBP) is extensively used in the extraction of U and Pu in the 'Purex' process (Wai and Wang, 1997). These reagents are considered to be technologically very important within the nuclear industry. These organophosphorus reagents are known to form coordinative solvated salts with lanthanides and actinides through the P=O group (Wai *et al.*, 1997).

TBP is neutral and trivalent lanthanides ions are not extractable by supercritical CO_2 without counteranions, but the extraction efficiencies are increased when TBP is mixed with tta (Wai, 1996). A strong synergistic effect was observed in the SFE of lanthanides and actinides from solid samples when a mixture of tributylphosphate (TBP) and fluorinated β-diketones was used (Lin *et al.*, 1995). According to Lin et al. (1995) and Luque de castro and Tena (1996), TBP has the ability to compete with the solid matrix for the unoccupied coordination sites by forming adducts with the lanthanide and actinide-β-diketone complexes in SC CO_2, making them easier to move from the solid phase into the fluid phase.

Macrocyclic ligands:

Macrocyclic polyethers (crown ether) are a class of selective ligands, which form stable complexes with metal ions based primarily on the ionic radius-cavity size compatibility concept (Wai *et al.* 1997). Substituting ter-butyl group at the benzene ring can significantly increase the solubility of macrocyclic ligands in SC CO_2. The solubility is also increased in methanol modified CO_2 (Wang *et al.* 1995).

2.4.2 Solubility of metal chelates in supercritical fluids

A key factor in supercritical CO_2 extraction of metal complexes from different matrices is a reasonable solubility for the metal chelate in supercritical CO_2 (Khorassani *et al.*, 1997). The solubilities of metal chelates in the SCFs play a key role in determining the efficiency of SFE of metal ions from aqueous phase and relatively inert solid matrix (Wang *et al.*, 2003). The solubility of metal complexes increases with increasing oxidation state of the metal atom, that is with increasing number of ligands per complex molecule and this is due to a better charge distribution in the complex with a higher number of ligands (Aschenbrenner *et al.*, 2007). Fluid pressure is an essential parameter in SFE because fluid density is directly related to the pressure. As the density of CO_2 is increased with an increase in pressure and the solubilizing ability of SC CO_2 increased leading to an increase of the solubility of a metal chelate in SC CO_2, which is beneficial to extraction. When the temperature is increased, three kinds of functions compete with each other. Higher temperature increases the heat motion of solutes on active sites of the matrix, which help the solute to lessen the adsorbing energy and to desorb more efficiently from the matrix (Lui *et al.*, 2001). According to thermodynamics, increase temperature increases the vapor pressure, which allows the solute to dissolve more easily in SC CO_2 (Wang *et al.,* 2002). However, the decrease in density caused by increases in temperature decreases the solubilizing ability of SC CO_2 and in turn the solubility of metal chelates in supercritical CO_2 (Lui *et al.*, 2001).

Wide ranges of solubilities have been observed for metal complexes, the solvation of which is influenced by several parameters, including (Smart *et al.*, 1996): pressure and temperature of SCFs, modifier effects, ligand type, metal type, oxidation state of the metal and the ligand functional groups. Different metal chelates and their solubilities are presented below.

Metal dithiocarbamate complexes:

A widely used chelating agent for trace metal extraction is diethyldithiocarbamate (DDC) and the resulting metal-DDC complexes have limited solubilities. If fluorine is substituted for hydrogen in the DDC ligand, the resulting complexes exhibit significantly higher solubilities in SC CO_2 (Laintz *et al.*, 1992).

Formation of metal chelates depends on the formation constants and the concentration of the ligand (Wai *et al.*, 1997). Large formation constants have been observed for metal dithiocarbamates. The solubility of alkylammonium dithiocarbamates salts increase with the increasing length of alkyl chain. Under normal conditions the solubility of metal dithiocarbamate chelates is very low. Dithiocarbamates do not form complexes with alkaline and alkaline earth metals (Wai, 1992). This property makes them ideal chelating agents for soil extraction applications where strong interference from alkaline and alkaline earth metals exists and specificity towards heavier metals is required in order to keep the chelating agent load low (Yazdi and Beckman, 1996).

Laintz *et al.* (1991) measured the solubility of different metal diethyldithiocarbamate (DDC) and bis-(trifluoroethyl) dithiocarbamate (FDDC) complexes in SC CO_2. The solubilities values for $Cu(DDC)_2$ and $Cu(FDDC)_2$ are 1.1×10^{-6} and 9.1×10^{-4} at 50°C and 10.1 MPa. Fluorination of DDC can enhance the solubilities of the resulting metal chelates in SC CO_2 by 2 to 3 orders of magnitude (Wai *et al.*, 1997). Wang and Marshall (1994) showed that increasing the chain length of the ligand substituents, (e.g. by substituting the two ethyl groups in DDC with two butyl groups) can also increase the solubility of the resulting metal chelates in SC CO_2 (Wang and Marshall, 1994). Changes in density (pressure) of supercritical CO_2 at a given temperature can significantly enhance the solubility of metal dithiocarbamate chelates (Wai *et al.* 1997; Smart *et al.*, 1997).

Metal β-diketones:

β-diketones are extensively used in the SFE of lanthanides, actinides and some transition metals (Wai *et al.* 1997). The fluorinated β-diketones usually form very soluble metal complexes in SC CO_2 and are more effective in the SFE of the f-block elements (Wai, 1995; Lin *et al.*, 1994). M'Hamdi *et al.* have studied the solubilities of $Cu(acac)_2$ and $Y(acac)_2$ in supercritical CO_2 and found the solubilities to be 0.37 and 0.82 g/L, respectively at 170°C. Saito *et al.* have studied acetylacetone complexes of Ga, In, Zn, Mn, Co, Cu and Li at 60°C and 29.4 MPa. The solubilities were 3.01, 2.63, 1.26, 1.01, 0.62, 0.40, 0.25, 0.21 and 0.01 mg/L, respectively. The solubility of the metal complexes at 60°C is much lower than those observed at 170°C. Lagalante *et al.* have studied the solubility of copper β-diketones and chromium β-diketones. These authors noted that metal complexes of the fluorinated β-diketones always have higher solubilities than the non-fluorinated β-diketone complexes.

Metal complexes with organophosphorus reagents:

Organophosphorus reagents have been used for the extraction of metals in SC CO_2. When organophosphorus reagents such as Cyanex are used for metal (Cu^{+2}) extraction with SC CO_2, the solubility of the metal chelate increases with the pressure (Wai and Wang, 1997). The solubilities of Cu complexes with Cyanex reagents in CO_2 increase with pressure, e.g. the solubility of Cu-Cyanex 301 complex is 7.83 g/L at 30.4 MPa and 0.9 g/L at 20.3 MPa (Wai and Wang, 1997). Since reasonable solvent loading of the SCF phase will be essential to achieve industrial-scale extractions (Smart *et al.*, 1997).

2.4.3 Effect of water and pH

The efficiency of metals extraction using *in-situ* chelation-SFE method increases significantly when a small amount of water is added to a matrix (Wai *et al.*, 1997). It is believed that water facilitates the metal chelation and serves as a modifier by blocking the active sites of the matrix, and thus reducing the adsorption of metals by the active polar sites of the matrix (Knipe *et al.*, 1991). Water can also substitute for metal in matrix coordination sites and facilitate the migration of the metal complex from the solid matrix into the fluid phase. Another important factor is the pH: the equilibrium pH of water is 2.9 under normal conditions of SFE if SC CO_2 is used, which is due to the formation and dissociation of carbonic acid and this pH can affect the formation of metal chelates under normal SFE conditions (Toews *et al.*, 1995). The formation of metal chelates depends on the pH e.g. dithiocarbamates can extract metal ions in water from pH 2-8 (Wai, 1991)

2.4.4 Temperature and pressure of the SCF

Thermodynamic conditions of temperature and pressure (SCF density) are the main factors affecting a SFE process. The SCF pressure in the extraction cell has a decisive effect on the efficiency of extraction (Wai *et al.*, 1997). In general, an increase in pressure will increase the density of supercritical fluid and thus increase the solubility of ligands and metal chelates, and therefore increases the extraction efficiency of metals. The temperature also has an effect on the analyte volatility, extraction kinetics and supercritical fluid density. By increasing the temperature at a certain value of pressure, the vapor pressure of solutes increases (Abd El-Fatah *et al.,* 2004). However, the increase in extraction efficiency due to an increase in analyte volatility and improved extraction kinetics can be countered by the decreased density (Wai *et al.*, 1997). As temperature increases, the metal chelate volatility and desorption from soil increases while the SCF density decreases and hence the metal chelate solubility also decreases (Saldana *et al.*, 2005).

2.4.5 Chemical forms of metal species

Metals can exist in soil as organometallic compounds, ionic species, and inorganic compounds such as oxides, sulfides. SFE of metals is therefore more complicated than that of organic compounds (Wai *et al.*, 1997). Some forms of metal species or compounds cannot be extracted by the ligands used in SFE. Organometallic compounds are usually soluble in SCFs, therefore they may be extracted without a ligand. This indicates that a sequential extraction could be used to first extract organometallic compounds and then the inorganic compounds by adding a chelating agent (Wai *et al.*, 1993).

2.4.6 Soil type

Soil properties that affect the SFE process include the soil type (i.e. the relative amount of sand, silt and clay), surface area, particle size, organic matter content and soil moisture content (Tomasko *et al.,* 1995). The nature of solid matrix is important in determining the extraction efficiency of organic compounds and metal complexes. The extraction efficiencies may be different for spiked solid support and the real soil samples. In the natural sample the analytes bind more strongly as compared to the spiked sample. This behavior makes it difficult to predict the behavior of a natural sample from the results provided by a spiked sample. The reason is that a spiked analyte coat the surface of natural sample and may not be located on the same sites as in case of a natural sample. The fractions of metals that cannot be extracted with SFE represent the unleachable metal in soil (Wai and Wang, 1997).

2.5 SUMMARY

A number of treatment technologies are used for soil remediation, in particular for metals-contaminated soil. Some of these techniques are still at their developmental stages while others technologies have not been commercialized yet but are promising. Some *in-situ* and *ex-situ* soil remediation techniques are presently used for the remediation of soil contaminated by organic and/or inorganic compounds. These two categories are than divided into technologies according to the mechanism employed; chemical, physical or biological and their application for organic or inorganic contaminations (United Nations, 2000).

Supercritical fluid extraction (SFE) is a promising new technology that may be used to remediate metal-contaminated sites. SCF has properties intermediate between those of a liquid and a gas, and has zero surface tension, which makes an SFE an attractive alternative to conventional liquid solvent extractions (Clifford *et al.,* 2001). As a result, there has been a lot of research done in order to investigate SFE for the remediation of contaminated soils. Although many of these studies focus on extracting organic compounds from soils, many recent studies have investigated the extraction of heavy metals and radioactive elements from soils using SCFs.

The most commonly used supercritical solvent is SC CO_2, since CO_2 is non-flammable, non-toxic, non-reactive and has moderate critical points of 31°C and 7.38 MPa, is available at low cost and is easily recycled (Wai *et al.*, 2001). Direct extraction of metal ions by SC CO_2 is highly inefficient because of the charge neutralization requirement and the weak solute-solvent interactions (Wai, 1995; Yang and Mathews, 2001)). However, when metal ions are chelated with organic ligands, they become quite soluble in SC CO_2 (Gopalan *et al.*, 2003). Supercritical CO_2 is used to extract metals from a variety of matrices by adding a suitable chelating agent.

The solubilities of metal chelates in a supercritical fluid play a key role in determining the efficiencies of SFE of metal ion from aqueous phase and relatively an inert solid matrix (Wang *et al.*, 2003). A wide range of solubilities have been observed for metal complexes, the solvation of which is influenced by several parameters, including pressure, temperature, modifiers, ligand used, and the type of metal to be extracted.

Limited studies have investigated the extraction of metals from soils. The objectives of this work are therefore to:

- modify the SFE experimental setup and to develop methods to allow the study of copper extraction from soil using SFE.
- determine the extraction efficiency of copper from an artificially contaminated sand and silt using a mixture of thenoyltrifluoroacetone (tta) and tributylphosphate (TBP) as the chelating agent.

CHAPTER 3 Material and Methods

This chapter describes the materials and methods used to evaluate the extraction of copper from soil using SFE with thenoyltrifluoroacetone (tta) as a chelating agent.

3.1 MATERIALS

The following section outlines the materials and chemicals used for this research work.

3.1.1 Soil

Two types of soil were used in the extraction experiments during the research: sand and silt. The sand was categorized as Sil 1 (60-100) of effective size 0.15 mm and was purchased from Sil Silica Inc. (Edmonton, AB). The particle size analysis for the sand is given in Table 3.1. The second soil was Devon silt, which was obtained from Geotechnical Group in the Department of Civil and Environmental Engineering at the University of Alberta. The silt was first homogenized by grinding in a grinding machine in the Geotechnical lab. The clay fraction was removed by sieving through U.S. mesh no. 100 & 200 Sieves. The particle size analysis of the silt is given in Table 3.2 and is presented graphically in Appendix A.

Table 3.1 Sieve analysis for sand

Metric sieve retained	U.S. mesh no.	Percent
8.000	5/16”	
6.350	¼”	
4.750	4	
2.960	8	
2.000	10	
1.180	16	
0.850	20	
0.600	30	0
0.425	40	0-1
0.300	50	4-14
0.250	60	15-36
0.180	80	35-50
0.150	100	5-15
0.106	140	5-15
0.075	200	0-2
0.053	270	
0.045	325	

Table 3.2 Sieve analysis for Devon silt

Metric sieve	U.S. mesh no.	Percent retained
0.150	100	0
0.075	200	91

Specific gravity = 2.68

3.1.2 Chemicals

For the extraction of copper, copper nitrate trihydrate (99%, ACROS organics, Fisher Scientific, Nepean, ON) was used to spike the soil. Thenoyltrifluoroacetone (99%, ACROS organics, Fisher Scientific, Nepean, ON) was used as a chelating agent to produce a soluble metal complex with copper. Tributylphosphate (TBP) (99%, ACROS organics, Fisher Scientific, Nepean, ON) was also used in some experiments. Their chemical formulas and molecular weights are given in the Table 3.3.

Table 3.3: Molecular weights and chemical formulas

Chemical	Formulae	Molecular weight
Copper(II)nitrate trihydrate	$Cu\ (NO_3)_2.\ 3H_2O$	241.60
Thenoyltrifluoroacetone	$C_8H_5F_3O_2S$	222.18
Copper(II)thenoyltrifluoroacetone	$Cu(C_8H_5F_3O_2S)_2$ or $C_{16}H_8F_6O_4S_2Cu$	505.90
Tributylphosphate	$C_{12}H_{27}O_4P$	266.32

All extractions were carried out using 4.5 supercritical grade carbon dioxide obtained from Praxair (Edmonton, AB).

Methanol (Electronic grade, ACROS organics, Fisher Scientific, Nepean, ON) was used for different purposes. It was used to clean the extraction vessel. It was also pumped into the SFE system through HPLC pump to avoid plugging of the metering valve. In the trap vials, methanol was used to collect $Cu(tta)_2$.

Nitric acid (Trace metal grade, Fisher Scientific, Nepean, ON) was used for the acid digestion. Copper and germanium (99%, ACROS organics, Fisher Scientific, Nepean, ON) were used as external and internal standards for the analysis of samples by inductively coupled plasma mass spectrometry (ICP- MS).

3.1.3 Extraction Vessel

A stainless steel, 300mL bolted closure vessel purchased from Autoclave Engineers (Division of Snap-Tite Inc., Erie, PA) was used for the extractions. The vessel and its parts are schematically shown in the Figure 3.1 and 3.2. An insulated jacket around the vessel is used to circulate water at the desired temperature for the extraction. The stainless steel vessel consists of the body, seal ring (gasket), cover and socket head cap screws. The vessel enclosure diameter is 1.81" (45.9mm). The vessel cover and the socket head cap screws are permanently attached to the bolted system. There are four 1/8" NPT openings on the cover as shown in the Figure 3.1. These are designated as C, B, J and E and they are located opposite each other. Openings C and G were used as inlet and outlet ports and J was used for the thermistor probe (OD YSI 406 thermistor probe manufactured by the Electrical group in the Department of Civil and Environmental Engineering at the University of Alberta). There is an opening, K, in the center of the cover in which a MagneDrive^{TM} mixer is installed.

The vessel was assembled according to the manufacturer's suggestions (Autoclave Engineers 2002). 1/16" stainless steel tubing was used for connections throughout the assembly. Two 1/16" to 1/8" NPT bored through stainless steel male connectors were placed at the outlet and inlet positions, which allows the 1/16" OD (0.05mm ID) stainless steel tubing to continue to the bottom of the vessel. Silane treated glass wool was used to plug the outlets C and B to prevent the entrainment of soil particles during extractions. A Teflon O-ring was placed between the vessel and the cover.

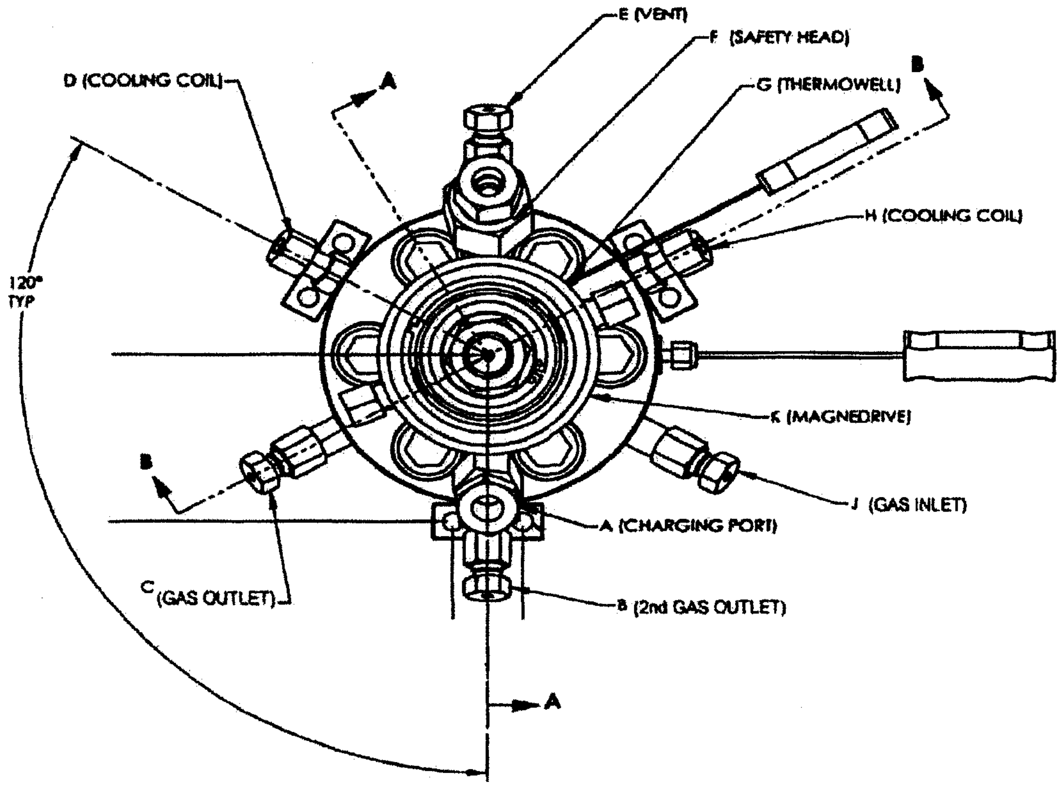


Figure 3.1: **Pressure vessel cover (adapted from Autoclave Engineers, 2002)**

The cover was then placed on top in a way that the openings for the screws on the cover and the vessel body were properly aligned. Jet-Lube MP-50 Moly-paste (Jet-Lube of Canada Ltd., Edmonton, AB) was used as a lubricant for the bolt's threading and the bolt openings. The bolts were threaded down into the vessel body using an Allen wrench. Then, the screws were tightened with a torque wrench in the following sequence: tighten them in a star pattern at a torque of 25ft-lb$_f$ then repeat the tightening at a torque of 35ft-lb$_f$ and 40ft-lb$_f$.

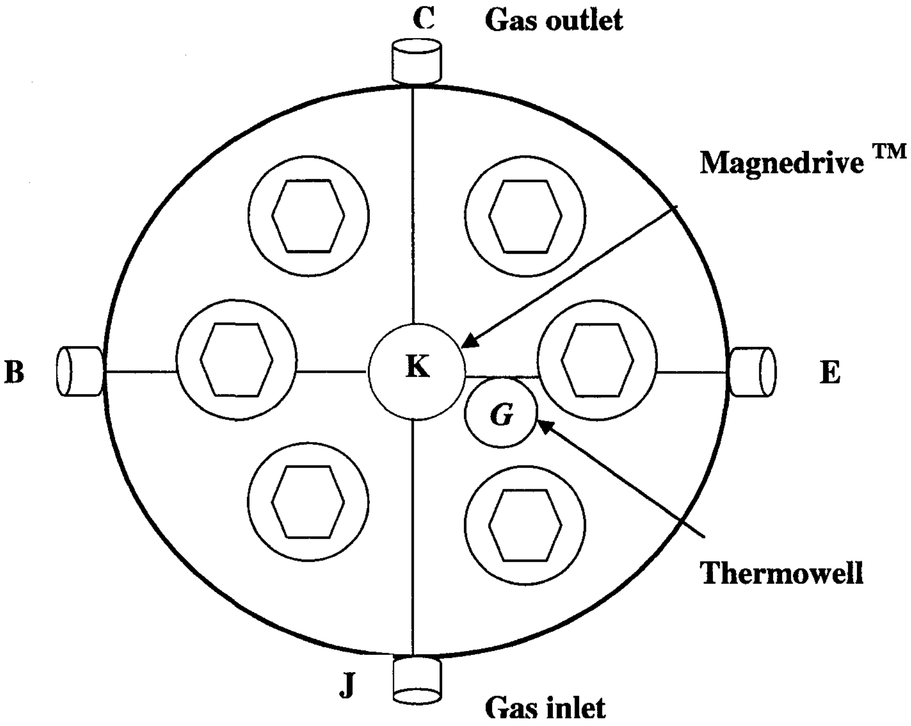
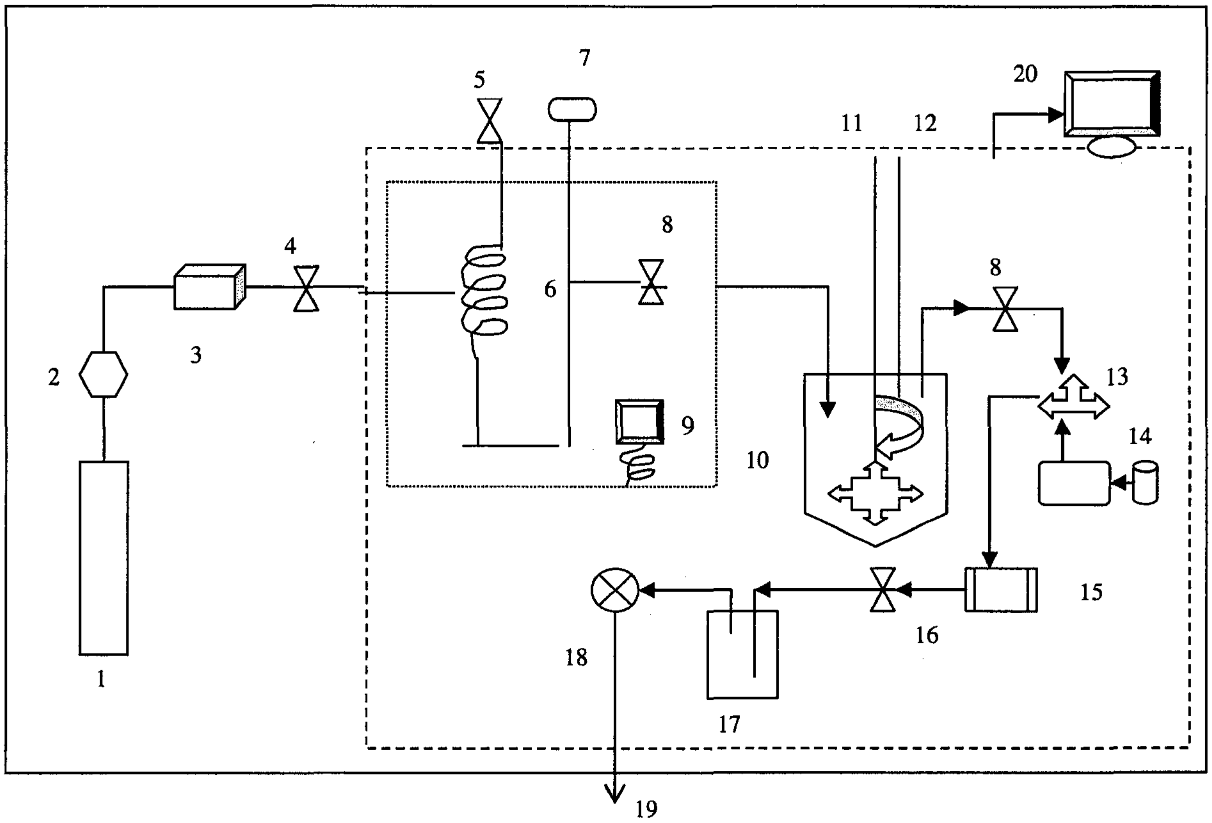


Figure 3.2: Schematic of pressure vessel cover

3.1.4 SFE System

The schematic of the SFE system is presented in Figure 3.3 and a photograph of SFE system used in this work is shown in Figure 3.4. The major components, suppliers and other ratings are given in Table 3.4.



1. CO_2 cylinder
2. Filter
3. ISCO syringe pump
4. Check valve
5. Pressure relief valve
6. Preheating coil
7. Pressure transducer
8. Three way ball valve
9. Heated circulating water bath
10. Extraction vessel
11. Impeller
12. Thermocouple
13. Peek mixing tee
14. Methanol pump
15. UV-Vis Detector
16. Metering valve
17. Traps
18. Gas flow meter
19. Vent to fumehood
20. Data acquisition

Figure 3.3: Supercritical fluid extraction (SFE) apparatus

Table 3.4: Supercritical fluid extraction components

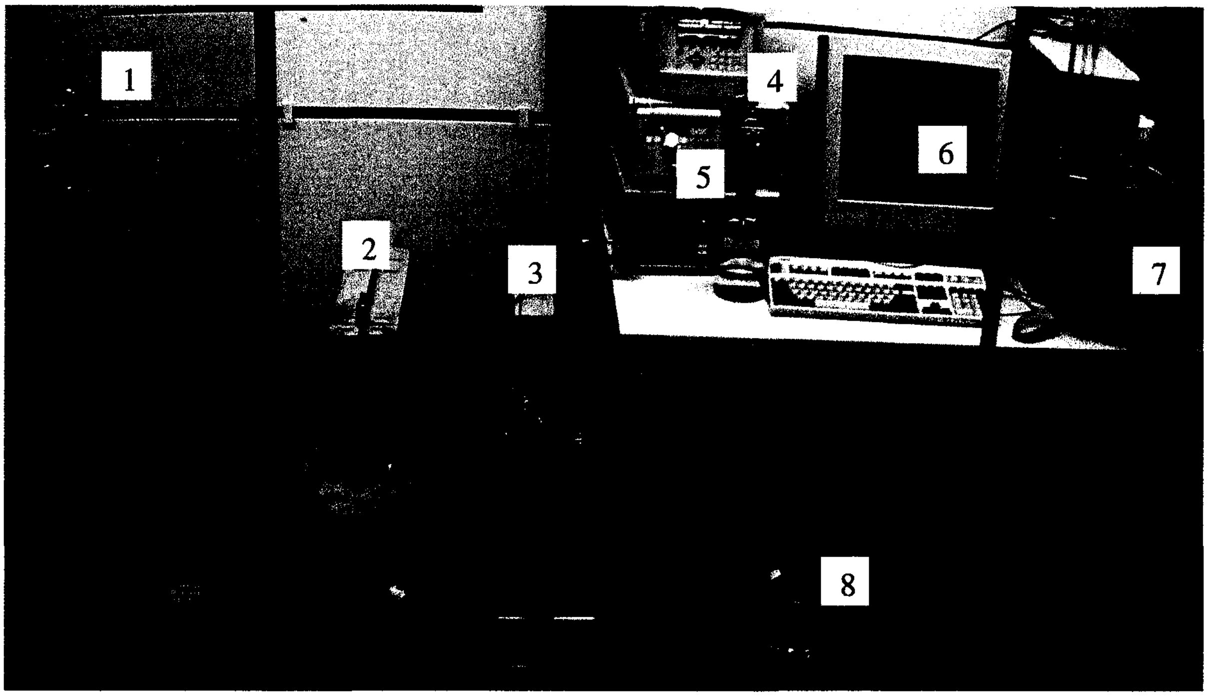
Component	Supplier	Pressure rating (MPa)
Liquid CO_2 Cylinder	Praxair Canada, Inc. (Edmonton, AB)	4.8
Filter (0.5 micron and 10 micron)	Edmonton Valve and fitting (Edmonton, AB)	
Syringe pump (ISCO 500D)	Canberra Packed (Mississauga, ON)	25.9
Pressure relief valve (SS-4R3A)	Edmonton Valve and fitting (Edmonton, AB)	25.5
Check valve (Nupro)	Edmonton Valve and fitting (Edmonton, AB)	41.4
Ball valve (Whitey)	Edmonton Valve and fitting (Edmonton, AB)	17.2, 41.4
Pressure transducer (PX 502)	Omega (Laval, QC)	20.7
Vessel (300ml, bolted closure)	Autoclave Engineers (Division of Snap-Tite Inc., Erie, PA)	37.2
Thermistor prob (YSI 406)	Labcor Technical Sales, Inc. (Concord, ON)	
Heating circulator (HAAKE DI)	Fisher Scientific (Nepean, ON)	
PEEK Mixing tee	Fisher Scientific (Nepean, ON)	
Metering valve (Nupro)	Edmonton Valve and fitting (Edmonton, AB)	41.4
Connectors, tees, etc.	Zimco Inc. (Calgary, AB)	27.6
PEEK tubings (1/16")	Fisher Scientific (Nepean ON)	
155 Gilson UV-VIS detector	Mandel Scientific Company Ltd. (Guelph, ON)	
ELAN 9000 ICP-MS	Parkin Elmer SCIEX instruments	

The CO_2 cylinder at a pressure of 5.68 MPa supplied the supercritical CO_2 used for the extractions. CO_2 was first filtered and then passed through one of two ISCO 500D continuous syringe flow pump, where it was pressurized to the desired pressure. The pump heads were cooled to a temperature of 7.5°C by circulating refrigerated water through temperature control jackets. After leaving the pump, the pressurized CO_2 flowed through 1/16" OD stainless steel tubing to a check valve. It then passed through a heating coil, a mixing tee, a three way ball valve and finally to the extraction vessel. The pressure relief valve on the vessel was set at 17.2 MPa to ensure that the pressure in the vessel never exceeded the set maximum value. The three-way ball valve was used to allow the flow either to the extraction vessel or to the bypass line. The pressure transducer was used to monitor the pressure inside the extraction vessel. The three-way valve is followed by a check valve and this check valve stops any backflow of CO_2.

CO_2 leaving the extraction vessel flowed through PEEK tubing to the second three-way ball valve. This valve ends the separation between the main line and the bypass line. After leaving the three-way ball valve, CO_2 entered a PEEK mixing tee, where it was mixed with methanol. A HPLC pump was used to pump methanol to the PEEK mixing tee. The CO_2 mixed with methanol flowed through the PEEK filter and then passed through the on-line UV-VIS detector, where the absorbance was measured. After passing through the UV-VIS detector, CO_2 flowed out through the heated metering valve to depressurize the CO_2. The metering valve was heated to 70% of the heating capacity of the rheostat to avoid the plugging of the valve.

After passing through the metering valve, the depressurized CO_2 flowed through methanol traps (in an ice bath) to collect the metal chelates. The CO_2 finally flowed through the gas flow meter and from there it was vented into a fumehood.

Water in a water bath was heated to the desired temperature and was circulated through the insulated heating jacket of the vessel in order to heat the vessel to the desired temperature. Inside the vessel, a thermistor probe was used to monitor the temperature. A MagneDrive™ mixer and impeller were used to stir mix the soil samples.



1. ISCO Syringe pump
2. MagneDrive™ mixer.
3. Thermostate
4. HPLC pump
5. US-VIS detector
6. Data acquisition
7. Gas flowmeter
8. Methanol trap

Figure 3.4: Lab-scale supercritical extraction (SFE) apparatus

A Lab VIEW 5.1 (National Instruments, Austin, TX) data acquisition program was used for data acquisition by a computer. All the information and data for the pressure (from the pumps and pressure transducer), temperature (as measured by thermistor probe), flow of CO_2 (as measured by the pumps), and absorbance (from the UV-Vis detector) were collected using Lab VIEW 5.1 software.

3.2 METHODS

This section highlights the procedures used for the SC CO_2 extractions of copper from spiked soils and the analysis of soil samples before and after extractions as well as the analysis of solvent traps.

3.2.1 Soil Preparation

For Copper extraction, part of the homogenized soil was spiked with a solution of Cu $(NO_3)_2$, in order to achieve an equal distribution. The silt and sand was spiked with Cu $(NO_3)_2$ to approximately 80 mg Cu^{+2}/ kg soil. After spiking the silt and sand was dried in an oven at 75°C and the big chunks of silt were then grounded by using a grinder in the Geotechnical lab.

3.2.2 Supercritical Fluid Extractions

Extraction experiments were performed at conditions given in the Table 3.5. Three experiments were conducted at each condition of temperature and pressure except one in which a mixture of (tta + TBP + 10% H_2O) was used.

The experimental conditions used in this work were chosen based on recommendations by Savoie (2002). In this research, higher pressures (ranging from 17.4 MPa to 24.1 MPa) and temperatures of 35°C and 40°C were tested based on the results of Savoie (2002). A chelating agent mixture i.e. tta + TBP was also tested here, as recommended in the previous work by Savoie (2002).

Table 3.5: Extraction experimental conditions

Spiked Soil	Ligand	P (MPa)	T(°C)	# of Exp.
Sand	tta	17.4	40	3
	-	20.6	40	3
	-	24.1	35	3
	tta + TBP	24.1	35	3
	tta + TBP +10%H_2O	24.1	35	1
Silt	tta	17.4	40	3
	-	20.6	40	3
	-	24.1	35	3
	tta + TBP	24.1	35	3
	tta + TBP +10%H_2O	24.1	35	1

The procedure for the extractions is summarized as follows:

- place approximately 50 g of spiked soil in the extraction vessel;
- add reagents (either tta and/or TBP) to the spiked soil in the extraction vessel;
- put glass wool in the outlets of the vessel cover and bolt the cover to the vessel;
- connect the inlet and outlet tubing to the vessel;
- fill water bath and heat the system to the desired temperature;
- pressurize the system to the desired pressure by flowing CO_2 into the vessel and start the mixer at 20 rpm;
- when the desired pressure and temperature are reached, the static period i.e. flow of CO_2 is started;
- a static period of 60 min was followed by a dynamic extraction i.e. flow of CO_2 of approximately 75 min in which $Cu(tta)_2$ is collected in methanol traps;
- after extraction, shut all valves, stop pumps, and depressurize the vessel;

- remove vessel cover and collect soil from the vessel and place into a glass jar for further analysis;
- analyze soil samples "before" and "after" the extractions for total copper by ICP-MS;
- calculate the extraction efficiency using copper concentration in the soil before and after the extraction; and
- analyze methanol traps for total copper by ICP-MS.

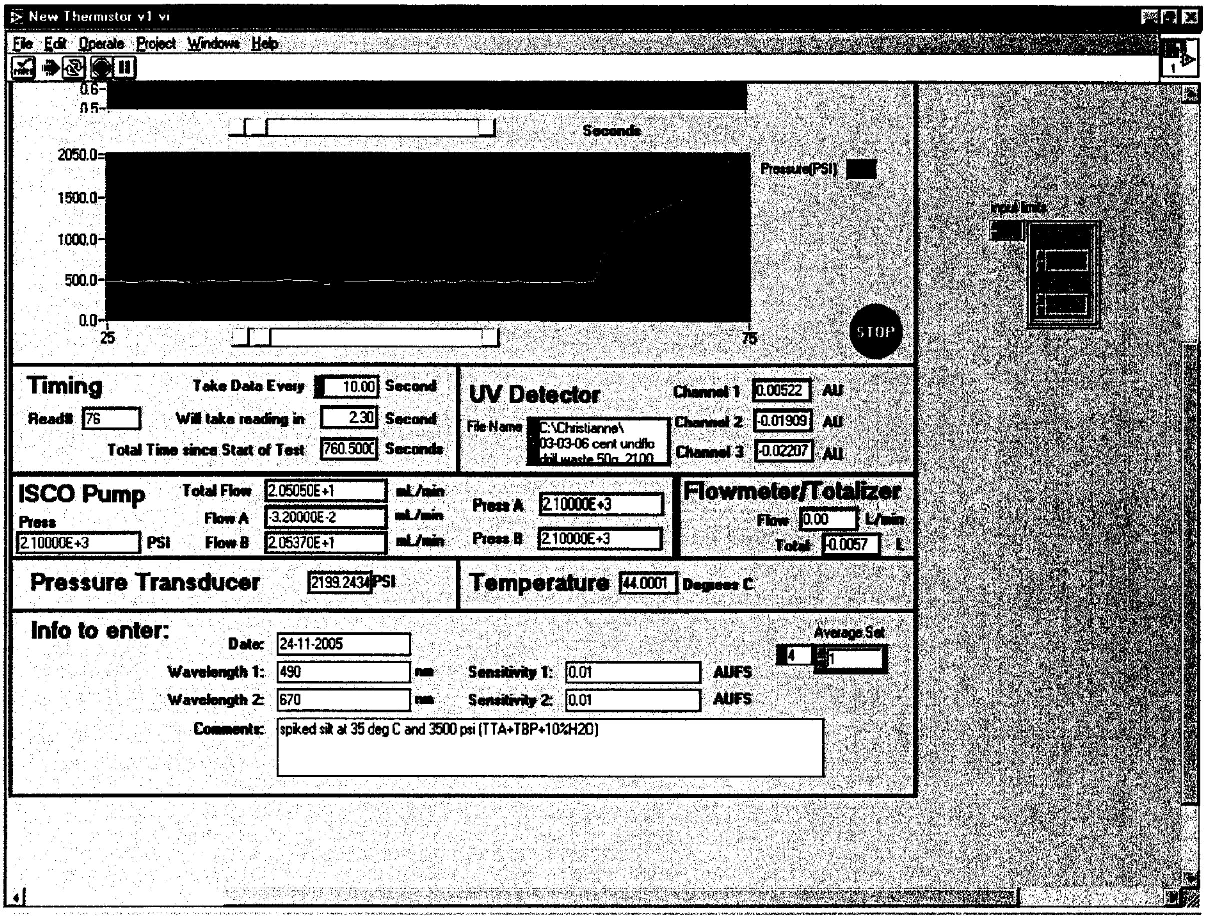
For extractions, 50 g of spiked sample was placed in the vessel. For the supercritical fluid extraction of copper it is necessary to form a complex with copper. For this purpose thenoyltrifluoroacetone is added in excess (10 times more) to form a complex with copper. For some extractions a mixture of ligands (i.e. TBP and tta) was added to the sample in equal molar concentrations. A mixer was used to mix the soil sample at 20 rpm, which was slow but sufficient to keep the sample stirred. A static extraction of 60 min was followed by 75 min dynamic extraction. The 75 min dynamic extraction time at SC CO_2 flowrate of 1 to 2 $mL.min^{-1}$ (at pump conditions of pressure and temperature) was used to ensure that the entire 300 mL of CO_2 in equilibrium with the metal complexes present in the soil completely flowed out through the traps. Methanol was added at 1 $mL.min^{-1}$ just prior to the metering valve to solubilize the $Cu(tta)_2$ contained in the SC CO_2 leaving the extraction vessel as it was removed from solution during depressurization.

$Cu(tta)_2$ was collected in the methanol traps and these solvent traps were analyzed to perform a mass balance. Soil samples were analyzed for copper before and after the extractions. Both solvent and soil samples were digested (see Section 3.2.4) and then were analyzed by ICP-MS. Extraction efficiency was then calculated based on the copper present in the soil before and after extractions.

3.2.3 Data Acquisition Using Lab View

National Instrument Lab View 5.1 performed the data acquisition. This software can be used for data acquisition, control, and analysis and presentation. This software uses a graphical programming development environment based on the G programming language (Savoie, 2002). The Lab View screen of the program is shown in the Figure 3.5. Roy Gitzell, a technician in the electronics group of Civil and Environmental Engineering at the University of Alberta developed this program. With this program, it is possible to save and average the data at different intervals. In the following experiments, data were collected every 10 seconds.

The variables being used and saved in the extraction experiments are shown in Figure 3.5. There is a section where comments can also be made, which can be saved in the Excel^{TM} file with all of the collected data in column format. The data consists of the scan number (or reading number, which is a serial number to identify the particular set of parameter values measured), time, pump pressure, pump flow, transducer pressure, vessel temperature, total pump flow, pump A flow rate, pump B flow rate, pump A pressure, and pump B pressure.



Timing

Take Data Every: 10.00 Second

Read#: 76

Will take reading in: 2.30 Second

Total Time since Start of Test: 760.500(Seconds

UV Detector

File Name: C:\Christianne\ 03-03-06 cent undflo drill waste 50g 2100

Channel 1: 0.00522 AU

Channel 2: -0.01909 AU

Channel 3: -0.02207 AU

ISCO Pump

Press: 2.10000E+3 PSI

Total Flow: 2.05050E+1 mL/min

Flow A: -3.20000E-2 mL/min

Flow B: 2.05370E+1 mL/min

Press A: 2.10000E+3

Press B: 2.10000E+3

Flowmeter/Totalizer

Flow: 0.00 L/min

Total: -0.0057 L

Pressure Transducer: 2199.2434 PSI

Temperature: 44.0001 Degrees C

Info to enter:

Date: 24-11-2005

Wavelength 1: 490 nm

Wavelength 2: 670 nm

Sensitivity 1: 0.01 AUFS

Sensitivity 2: 0.01 AUFS

Average Set: 4 1

Comments: spiked silt at 35 deg C and 3500 psi (TTA+TBP+10%H2O)

Figure 3.5: Lab view screen

3.2.4 Soil Sample Analysis

Soil samples were analyzed for total copper concentration using ICP-MS. Prior to analysis, samples must be digested using an appropriate sample preparation method. For copper analysis, samples were digested according to EPA standard method 3051 (Section 3.2.4.1) (U.S. EPA, 2001).

3.2.4.1 Sample Preparation for Analysis

Soil samples were digested by EPA Method 3051 (U.S. EPA, 2001). This method describes microwave assisted digestion of sediments, sludges, soils, and oils. The Milestone Microwave Laboratory System (ATS Scientific Inc. USA) in the Geo-environmental lab of the Department of Civil and Environmental Engineering at the University of Alberta was used for microwave digestion. The microwave digestion was carried out in the following manner:

- 0.5 g of a well-mixed sample was placed into the fluorocarbon digestion vessel;
- 10 mL of concentrated nitric acid was added to the vessel in a fume hood;
- the temperature of each sample was raised to 170°C in 10 min and remained between 170 and 180°C for the balance of 10 min period with a power of 1000W;
- a pressure of 0.8 ± 0.07 MPa was maintained in the digestion vessel;

- at the end of the microwave program, the vessels were allowed to cool for 20 min before removing them from the microwave unit to carefully vent and uncap them in a fume hood;
- the samples were filtered, diluted, and transferred to the centrifuge tubes; and
- the digested samples were stored before they were analyzed by ICP-MS.

For each digestion, a blank methanol trap and a blank soil sample was included with contaminated soil samples.

3.2.4.2 ICP-MS Analysis

ICP-MS was used to determine the total amount of copper in the solvent traps as well as in the soil samples. The soil samples (before and after extractions) and methanol traps were analyzed to evaluate the extraction efficiency.

Inductively coupled plasma mass spectroscopy (ICP-MS) was developed in the late 1980's to combine the easy sample introduction and quick analysis of ICP technology with the accurate and low detection limits of a mass spectrometer. The resulting instrument is capable of trace multielement analysis, often at the part per trillion levels. A Parkin Elmer ELAN 9000 ICP-MS (Parkin Elmer SCIEX instruments) in the Geo-environmental lab of the Department of Civil and Environmental Engineering at the University of Alberta was used for this purpose. The following section will discuss the start-up, optimization and sample analysis of the ICP-MS.

Operation

Starting the instrument:

- the ICP-MS instrument was warmed up and optimized. The instrument must run for at least 30 min with the plasma on before performing the optimization;
- check the peristaltic pump tubing. Let it run (dry) to align itself before clamping it onto the rollers. Then clamp the tubing onto the rollers, which rotate at 20 rpm and run some wash solution (1% or 2% HNO_3) through. Watch it closely until a good flow (low pulsation) is achieved;
- check the Argon gas to make sure it is sufficient for optimization and analysis (approximately need 17.3 MPa). Check the operating pressure of the chiller (should be ~ 0.4 MPa), the oil, and the drainage bucket (Prevent backpressure by ensuring the drainage bucket remains less than ½ full);
- before igniting the plasma, ensure that the peristaltic pump is off. If the system is running well, a very distinct popping sound can be heard upon ignition;
- start the peristaltic pump again, running wash solution (1% or 2% HNO_3) through it;
- let the plasma warm for 15 to 20 minutes before starting optimization;

Optimization

Optimization should be performed after instrument warm-up. In the computer a workspace is opened to perform each specific optimization procedure. Each optimization workspace is saved so that the information can be applied to the analysis. The daily optimization flow chart is given in the Figure 3.6.

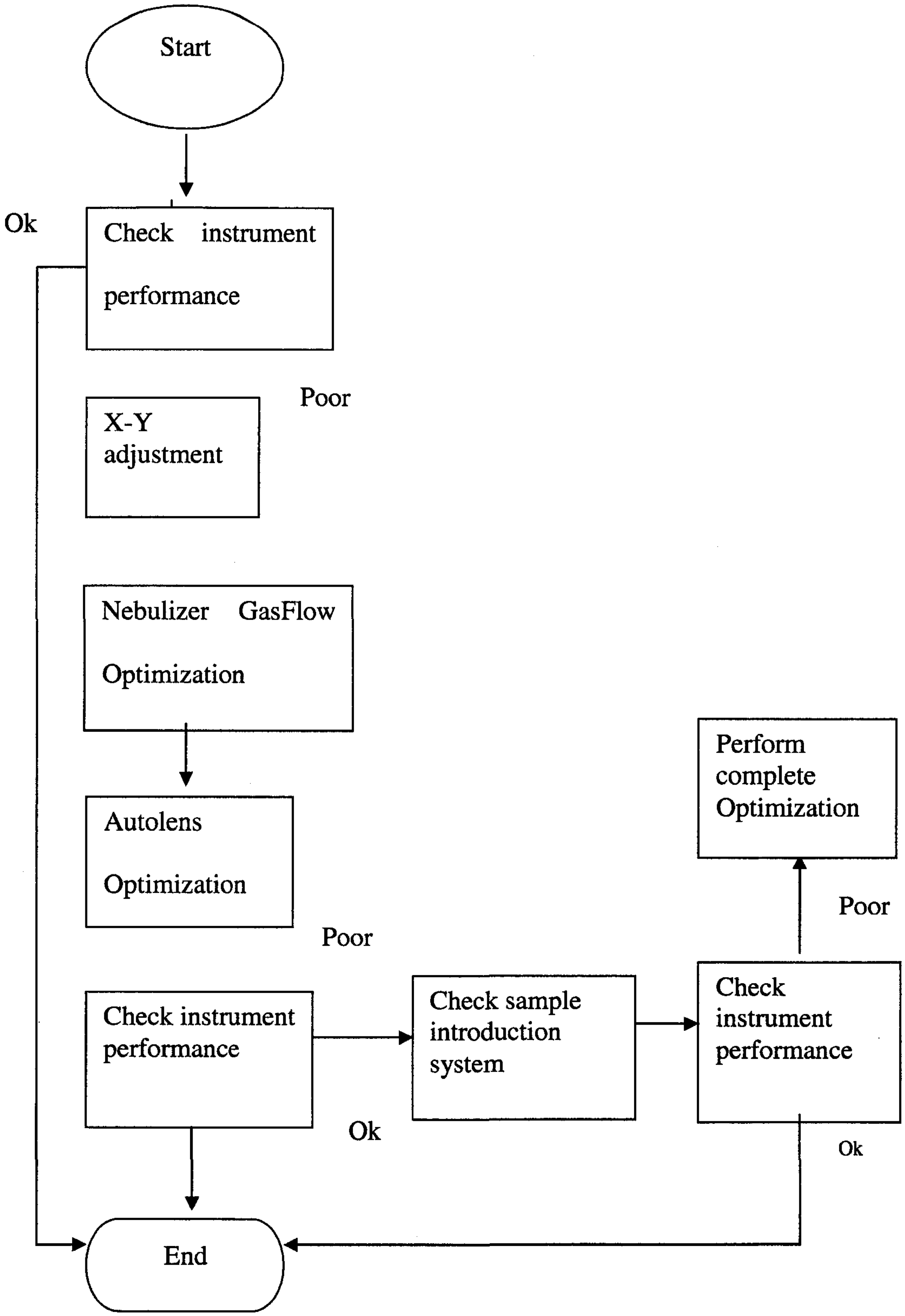


Figure 3.6: Daily Optimization Flowchart

The optimization steps are as follows:

- Tuning / Mass calibration – Tuning workspace and tuning solution is used to do the Tuning / Mass calibration. The measured mass for the specific isotope should be within 0.1 amu of theoretical values.
- Nebulizer flow rate – Nebulizer flow rate should be performed daily. When the flow is increased, the counts per second and the oxide levels are increased and the doubly charged species are decreased. Therefore these must be optimized. The flow should be ~ 0.9 – 1.0 L min^{-1};
- RF power – This should remain constant depending on the matrix of the material. For water samples a lower voltage (~1100V) is required than for the soil samples (~200V).
- Lens voltage – The optimization is performed on daily basis. The lens needs to be cleaned in order to focus at a higher voltage.
- Auto lens calibration – It should be performed when the lens voltage has changed by more than 0.25 V.
- Detector optimization – It should be performed every week or two. Check the dual detector. If the coefficients are not good (i.e. $R^2 \neq 0.9999$), complete the entire detector calibration.
- Daily performance check – This check should be performed daily and the values obtained can be compared with the target values in the Table 3.6. If the oxides are a bit high, lower the nebulizer gas flow slightly.

A complete instrument optimization must be performed when the state of the instrument is unknown. The ICP-MS instrument requires certain optimization procedures to be completed daily for peak performance and the samples should not run until the instrument performance has been verified. The performance criteria are given in the Table 3.6 in which the scan of the mass range shows the purity of DI water, purity of argon, background ion intensities, and contamination in the sample introduction system and on the cones.

Table 3.6: Typical ICP-MS performance specifications

Test	ELAN 9000	Test	ELAN 9000
^{24}Mg Sensitivity	>100,000 cps	Ba^{2+}/ Ba	< 0.03
^{115} In Sensitivity	>400,000 cps	CeO/Ce	< 0.03
^{238}U Sensitivity	>300,000 cps	Bg Level (Mass 220)	< 25cps
Precision	< 3%	Noise SD (Mass220)	< 5cps

cps = Counts per second Bg = Background level

Three different types of ELAN 9000 solutions (Parkin Elmer SCIEX instruments) were used for optimization:

1. ELAN 9000 setup/ stab/ Masscal solution (10 ppb Mg, Rh, Cd, Cu, In, Ba, Ce, Pb, U) was used for tuning/ Nebulizer Gas/ Lens voltage/ Pulse stage.
2. ELAN 9000 Detection limit solution (10ppb Be, In, U, Co) was used for optimizing Auto-lens.
3. ELAN 9000 Dual detector solution (200 ppb Mg, Cu, Rh, Cd, Pb and 2,000 ppb Be) was used for optimizing Analog stage and Dual detector cross calibration.

In the process of optimization, the nebulizer gas flow rate is a key parameter, because high flow rate may cool the plasma. This cooling, in turn, decreases the ionization efficiency and molecular ion formation is favored. On the other hand, low flow rate reduces the analyte introduction rate and the plasma may over heat. The target flow rate is ~ 0.9 – 1.0 L min^{-1} as specified previously.

Calibration of ICP-MS

Calibration is the fundamental part of acquiring the best data from the ICP-MS. External standardization involves measuring a blank solution followed by a set of standard solutions to create a calibration curve over the concentration range of interest. The instrument was calibrated by analyzing Cu standards of concentration 2ppb, 10pbb, 50ppb, and 100ppb. A 1 ppm working standard was prepared from copper stock solution of concentration 1000 $mg.L^{-1}$ (99%, ACROS organics, Fisher Scientific, Nepean, ON). The 1 ppm working standard was used to make further solutions of 2ppb, 10pbb, 50ppb, and 100ppb for which sample calculations are given in Appendix B1. Samples of unknown concentration were measured after the standards have been measured.

Another calibration technique is internal standardization. Internal standards are used to correct for changes in instrument hardware response or for sample-to-sample variations in sensitivity. An internal standard is a non-analyte isotope that is added to the standards and samples before analysis. The internal standard should be selected so that their masses do not interfere with the analytes and so that their masses match the mass(es) of analytes and internal standard should not be common environmental contaminants. For analyzing Cu, Ge (10 $mg.L^{-1}$) (99%, ACROS organics, Fisher Scientific, Nepean, ON) was used as an internal standard, since their masses are close to each other (Cu = 65 and Ge = 72), but Ge will not interfere with Cu and Ge is not commonly present in soil samples. Before starting the analysis, all blanks, calibration standards, and samples were spiked with 250 μL of internal standard (i.e. Ge at 10 $mg.L^{-1}$) and sample calculations are given in Appendix B2.

3.2.4.3 Analysis of Samples

To analyze samples of unknown composition by ICP-MS, it is necessary to adopt a stepwise analytical method in order to get accurate results. The following steps describe the procedure for a batch analysis:

1. complete daily setup and optimization procedures, as described previously;
2. prepare a sample list, designate and verify that Dataset file has sufficient entries available to hold all the data, which can hold results from up to 2000 samples, standards, or blanks;
3. prepare blanks, calibration standards, and samples required for the analysis;
4. place all blanks, standards, and samples into the autosampler tray according to the information in the sample and method file;
5. place the sample tubing in the blank solution;
6. when the blank determination is completed, place the sample tubing in the first standard solution;
7. place the sample tubing in the wash vessel and aspirate the solution;

8. repeat step 6 and 7 for all the remaining standards;
9. after measuring all standards, analyze all samples one by one; and
10. after measuring each sample, the sample tubing is placed in the wash vessel and aspirate the solution;

Once the samples have been analyzed, the ICP-MS must be shut down. The following steps must be followed:

- flush with wash solution (1% or 2% HNO_3) for a few minutes;
- stop plasma;
- stop peristaltic pump, loosen tubing;
- loosen autosampler pump tubing;
- turn off chiller; and
- leave vacuum running.

3.2.5 Solvent or methanol traps analysis

Solvent samples were also analyzed for total copper using ICP-MS. For ICP-MS analysis, solvent trap samples must be digested prior to analysis. These digestions were carried out according to EPA Standard Method 3010 A (U.S. EPA, 2001).

3.2.5.1 Sample Preparation for Analysis

The solvent samples were digested according to EPA Standard Method 3010A (U.S. EPA, 2001). This method was slightly altered because the aim was to break down the copper tta complex by lowering the pH. The filtration step was also eliminated. The procedure is summarized as follows:

- the solvent trap was diluted to 100 mL using ultra pure DI water and a 100 mL aliquot was transferred to a beaker;
- 3 mL of concentrated HNO_3 were added;
- a ribbed watch glass was placed on the beaker and the beaker was heated on a hot plate to evaporate to a low volume;
- the resulting solution was cooled and 3mL of HNO_3 was added;
- a watch glass was placed on the beaker and the solution was refluxed for 30 min;
- after cooling, the beaker walls and watch glass were washed down. The sample was collected into centrifuge tubes; and
- the digested samples were stored until analyzed by ICP-MS.

All of these steps were carried out in the fumehood. For each digestion, a blank was included.

3.2.5.2 ICP-MS Analysis

The solvent traps were analyzed by ICP-MS to determine the total amount of copper. ICP-MS, the operation, optimization and calibration of the ICP-MS were performed as described in Section 3.2.4.2.

3.2.5.3 Analysis of Samples

Digested solvent samples of unknown composition were analyzed by ICP-MS. A stepwise analytical method for sample analysis is described in Section 3.2.4.3.

3.2.6 Quality Control

Commercial analysis was done on copper samples to confirm the accuracy and the efficacy of the laboratory analysis method i.e. ICP-MS method. For this purpose, copper samples were sent to the Enviro-Test Laboratories Inc. (Edmonton, AB) for copper analysis. The results obtained in house at the University of Alberta and from the commercial lab for the copper samples were the same, thus confirming the accuracy of the ICP-MS method being used.

3.2.7 Extraction efficiency

The extraction efficiency can be calculated from the mass of the copper measured by the ICP-MS. The extraction efficiency of copper from soil was calculated for each extraction experiment. The equation used to calculate the extraction efficiency is given below in Equation 3.1 and a sample calculation is given in Appendix B3.

$$\text{EF\%} = \frac{M_b - M_a}{M_b} \times 100 \qquad (3.1)$$

Where,

EF = Extraction efficiency

M_b = mass of copper in the dry soil before the extraction

M_a = mass of copper in the dry soil after the extraction

CHAPTER 4 RESULTS AND DISCUSSION

In the following chapter, the results of the extraction experiments performed are described and discussed.

4.1 SC CO_2 EXTRACTION OF METALS FROM THE SOIL

Various studies have been done to obtain the optimal conditions for the extraction of metals from the solid matrices. In this work, all the extractions were done at a pressure ranging from 17.3MPa to 24.1MPa and at temperatures of 35°C and 40°C. These conditions were chosen, since they yield high SC CO_2 densities ranging from 0.8 to 0.9g.mL^{-1}. Pressures above 24.1MPa could not be tested due to the limitations of the syringe pumps used in the experiments.

The following sections provide the results obtained for all of the experiments done in this work. A sample Excel data file for an extraction experiment is provided in Appendix C.

4.1.1 Pressure data

There were two sets of pressure data collected from the system, one from the ISCO syringe pump and the other from the pressure transducer. In both cases, the pressure data were recorded by using LabView^{TM} data acquisition software. The syringe pump pressure (at pump A and B) represents the pressure at which the CO_2 is flowing into the vessel. The pressure transducer, on the other hand, indicates the pressure directly upstream of the vessel. Figure 4.1 shows the pressure data collected during the extraction at 20.7 MPa and 40°C.

The ISCO syringe pumps are designed so that they can be set either at a constant flowrate mode or at constant pressure mode. They were set at a constant pressure mode, so that the SC CO_2 flowed at a constant pressure despite of which pump is running. Both of the pumps (A and B) run independently and simultaneously. In the beginning, the pump pressure corresponds to the pressure of CO_2 cylinder, which is approximately 5.9 MPa. There is an offset in the pressure data collected from both the pressure transducer and the pumps. This offset explains why the transducer pressure is always 0.9 MPa higher than the pump pressure.

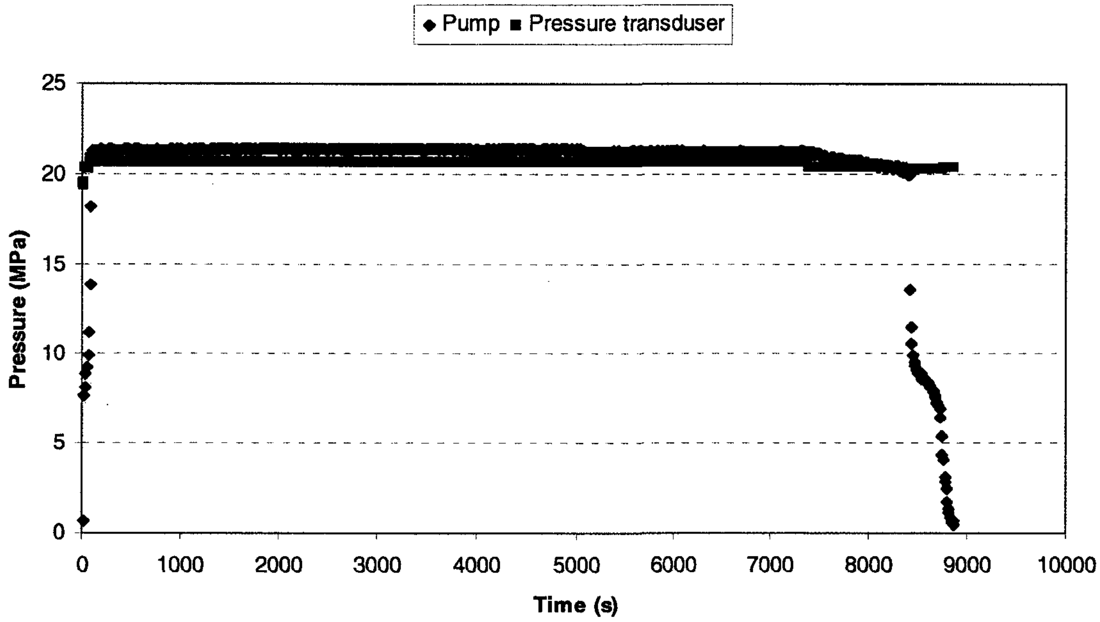


Figure 4.1: Sample pressure data for an extraction experiment at 20.7 MPa and 40°C

During the extractions, data acquisition by the LabView program begins, when both the pumps are refilled and pressurized to a desired pressure. When the pump is refilling, the pressure becomes the same as that of CO_2 cylinder pressure. The pump pressure rises very quickly to the desired pressure (set pressure in constant pressure mode) and stabilizes in seconds. In Figure 4.1 the pumps are pressurized to a desired extraction pressure of 20.7 MPa, Pump B runs first and the CO_2 flow was opened to the vessel at about 60.1s. The pressure in the vessel as measured by the pressure transducer rises gradually to 21.6 MPa and stabilizes. The transducer pressure was 0.9 MPa higher than the pump pressure and this offset is found to be in an agreement with the repeated observations in all extractions. Only pump B was used in all of the extraction in order to avoid any offset arising from switching the pumps.

According to Figure 4.1 the pressure in the vessel remains stable until the extraction is stopped at 8051s and the vessel is depressurized. The transducer pressure reading then returns to the original reading of 0.9 MPa.

4.1.2 Flow data

The flow data is collected from the ISCO syringe pump and is recorded by the LabView^{TM} data acquisition software. This flow data represents the flowrate at which CO_2 is flowing from the pumps at the desired pressure and at 7.5°C. Sample flow data is shown in Figure 4.2 for an extraction at 20.7 MPa and 40°C.

The maximum flowrate is 204 mL.min^{-1} at which CO_2 can flow from the cylinder to refill the pumps. The total flow in Figure 4.2 indicates the combined flow from Pump A and Pump B respectively. For the dynamic extractions, most extractions were carried out at a total flow of approximately 1 mL.min^{-1}.

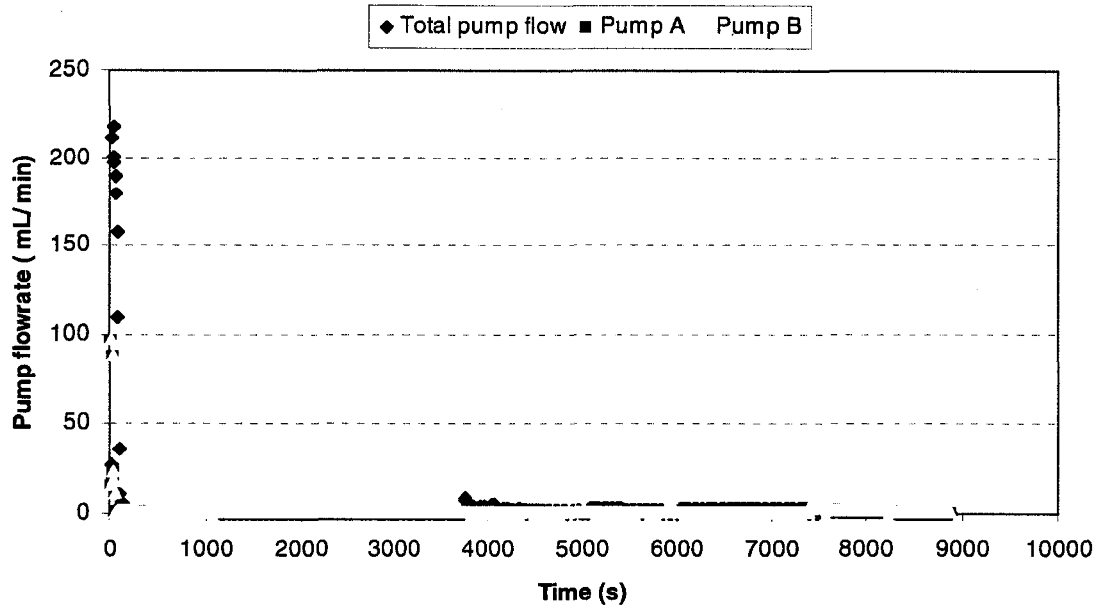


Figure 4.2: Sample flow data for an extraction experiment at 20.7 MPa and 40°C

The flow data were also confirmed using a gas flowmeter placed after the collection vials. The amount of CO_2 flowed through each vial was measured manually by a gas flowmeter. The gas flowmeter was hooked to a vial through rubber tubing and was operating at room temperature.

4.1.3 Temperature data

A thermistor probe was used to continuously monitor the temperature inside the vessel. The vessel was heated to the desired temperature by circulating hot water through an insulated jacket around the vessel. A thermometer was used to monitor the temperature in the water bath. The temperature data collected for an extraction experiment is presented in the Figure 4.3.

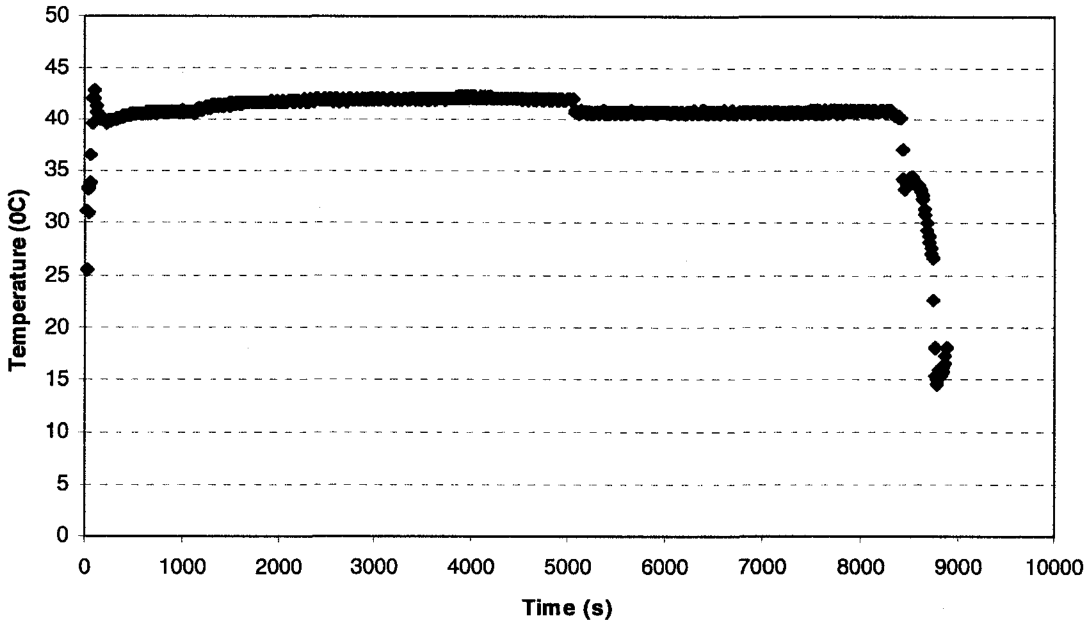


Figure 4.3: Sample temperature data for an extraction at 20.7 MPa and 40°C

The insulating jacket and circulating hot water allows performing extractions at different temperatures and adjustments can be made by simply adding ice to the water bath and lowering the heater set point of the water bath or by increasing the temperature by increasing the heater set point. The temperature in the vessel and the water-bath are the same, but the temperature rises up to approximately 4°C higher when the vessel is pressurized. The water bath temperature for the extraction experiment was 40°C as shown in the Figure 4.3. This change of temperature with the rise in pressure can be observed in all extraction and the same pattern was found by Savoie (2002). This increase in temperature is due to the sudden rise in pressure in the vessel. After this initial temperature rise, the temperature in the vessel gradually decreases to the set temperature of the water bath.

4.2 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

Once all the extractions have been completed, the soil samples and the liquid traps were further analyzed by ICP-MS. The copper concentration is very low in all samples, therefore, ICP-MS was chosen as the method of analysis. ICP-MS is a very powerful tool for *trace* (ppb-ppm) and *ultra-trace* (ppq-ppb) elemental analysis. ICP-MS is rapidly becoming the technique of choice in many analytical laboratories for the accurate and precise measurements needed for today's demanding applications. ICP-MS is an instrument of choice for metals analysis that provides a good sensitivity and requires less sample volume. Due to the specificity of ICP-MS, the results obtained are accurate and seldom require confirmation.

For analysis by ICP-MS, all samples were acid digested (microwave) by using an EPA SW-846 Method 3050 (for the soil). Microwave digestion prepares samples in less time (minutes rather than hours), uses less acid, and retains even volatile elements.

4.2.1 Calibration curves

Calibration is the fundamental part of acquiring the best data from ICP-MS instrument. External standardization involves measuring a blank solution followed by a set of standard solutions to create a calibration curve over the concentration range of interest. The instrument was calibrated by analyzing Cu^{+2} standards of concentration

2ppb, 10pbb, 50ppb, and 100ppb. The calibration curves for Cu (63) & Cu (65) are given in Figure 4.4 and 4.5 respectively.

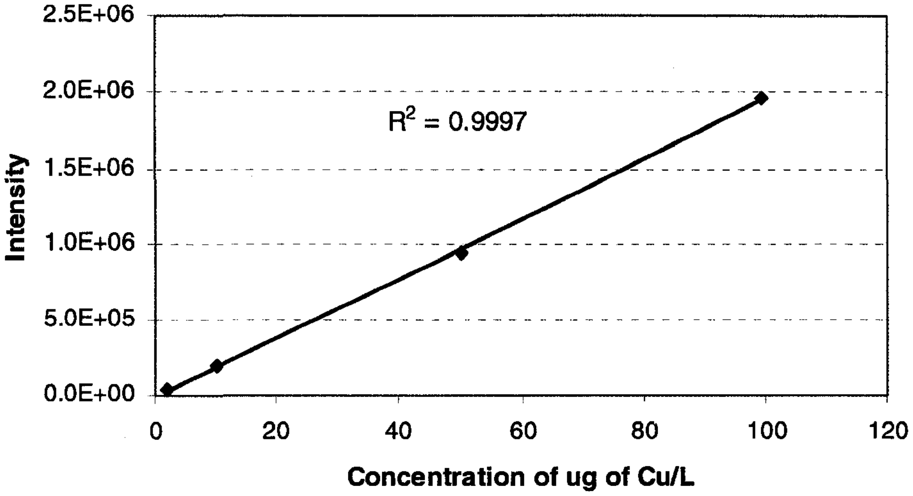


Figure 4.4: Calibration Curve for Cu (63)

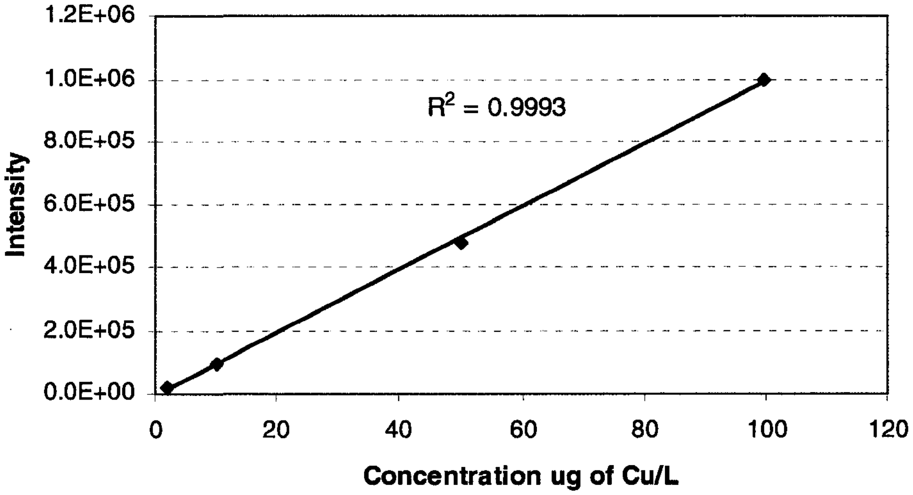


Figure 4.5: Calibration Curve for Cu (65)

4.2.2 Method Verification

Some standards of copper (II) triflouroacetylacetonate and copper (II) acetylacetonate were analyzed on ICP-MS to ensure the accuracy of the instrument. The results are given in Table 4.1 and 4.2, which shows that the accuracy is between 74%-97%.

Table 4.1: ICP-MS analysis of copper (II) triflouroacetylacetonate (Cu(tta)$_2$)

Theoretical Conc. (µg of Cu. L^{-1})	Average observed Conc. (µg of Cu. L^{-1})	% Accuracy	
34	29	85	S. D = 5.8 % R.S.D = 6.3
51	49	96	
68	66	97	
85	75	88	

Table 4.2: ICP-MS analysis of copper (II) acetylacetonate (Cu(acac)$_2$)

Theoretical Conc. (µg of Cu. L^{-1})	Average observed Conc. (µg of Cu. L^{-1})	% Accuracy	
48	44	92	S. D = 7.7 % R.S.D =9.0
58	43	74	
62	55	89	
72	62	86	

These results confirm that the results of the ICP-MS analysis are reliable for determining total copper from Cu(tta)$_2$ and Cu(acac)$_2$. The purpose of doing verification is to make sure that the digestion procedure works for our copper chelates. The second reason was the ICP-MS instrument, which was used to determine the concentration of Cu^{+2} in the methanol traps at the ppb level. In the previous research work done by Savoie (2002) a spectrophotometer was used for copper analysis.

4.3 SAMPLE ANALYSIS

The results for the soil samples and the traps are given in Appendix D. Generally in terms of efficiency, spiked sand extractions are more promising as compared to the spiked silt. In both silt and sand the concentration of Cu^{+2} with respect to time is decreasing and has the same trend at all conditions of temperature and pressure. Figure 4.6, 4.7 and 4.8 are the results for the spiked silt and 4.9, 4.10 & 4.11for spiked sand at three different pressures.

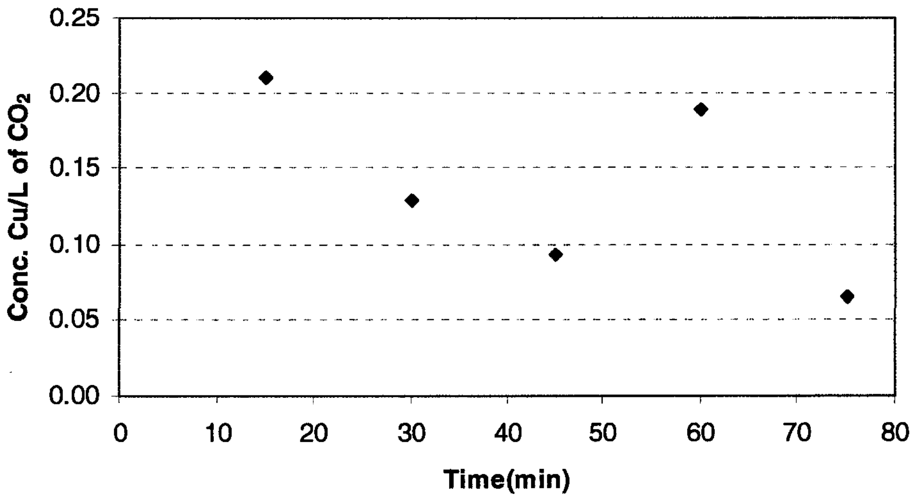


Figure 4.6: Concentration of total copper in the methanol traps as a function of time for an extraction of spiked silt soil (0.04 g of Cu^{+2}(50 g of silt) $^{-1}$) at 40^0C and 17.2 MPa

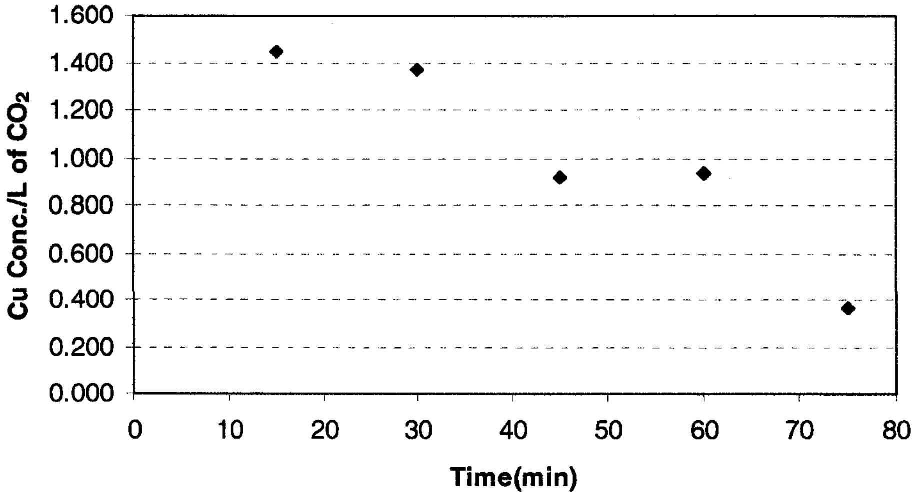


Figure 4.7: Concentration of total copper in the methanol traps as a function of time for an extraction of spiked silt soil (0.04 g of Cu^{+2}(50 g of silt)$^{-1}$) at 40^{0}C and 20.7 MPa

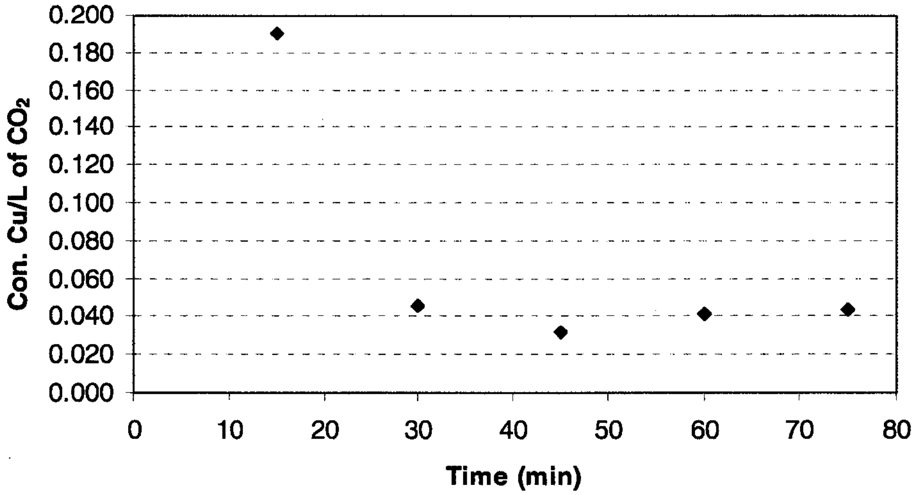


Figure 4.8: Concentration of total copper in the methanol traps as a function of time for an extraction of spiked silt soil (0.04 g of Cu^{+2}(50 g of silt)$^{-1}$) at 35^{0}C and 24.1 MPa

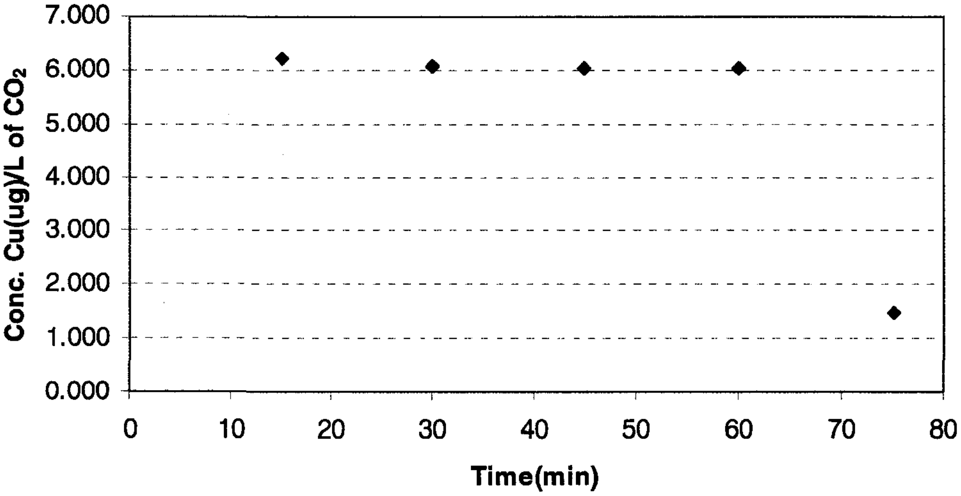


Figure 4.9: Concentration of total copper in the methanol traps as a function of time for an extraction of spiked sand soil (0.04 g of Cu^{+2}(50 g of sand) $^{-1}$) at 40^0C and 17.2 MPa

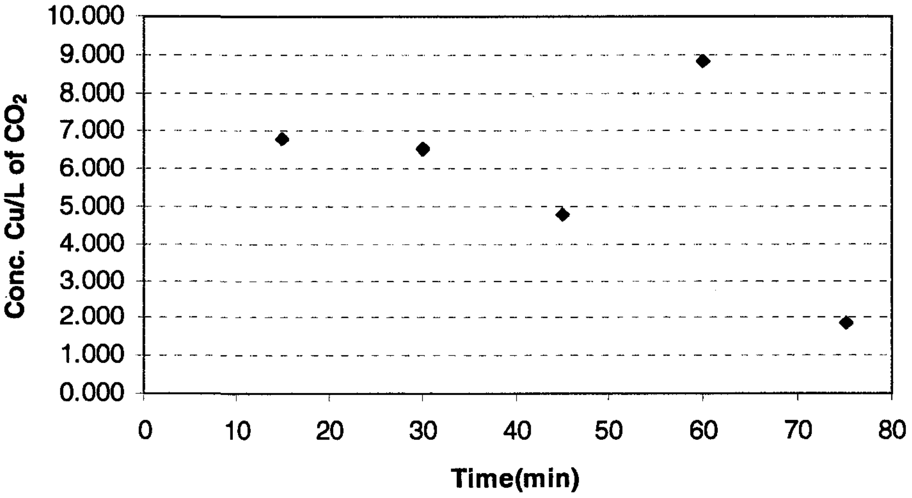


Figure 4.10: Concentration of total copper in the methanol traps as a function of time for an extraction of spiked sand soil (0.04 g of Cu^{+2}(50 g of sand) $^{-1}$) at

40^0C and 20.7 MPa

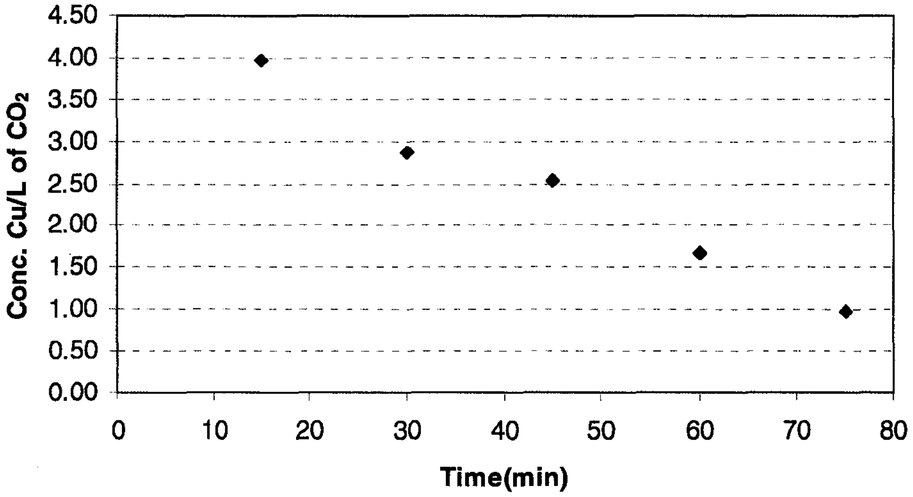


Figure 4.11: Concentration of total copper in the methanol traps as a function of time for an extraction of spiked sand soil (0.04 g of Cu^{+2}(50 g of sand) $^{-1}$) at 35^0C and 24.1 MPa

The results suggest that the concentration of Cu^{+2} in the traps is much less than the spiked concentration. On the other hand Cu^{+2} concentrations in the soil samples especially sand is sometimes lower or higher than the spiked concentrations. This can be explained by the fact that spiking was done with liquid $Cu(NO_3)_2$, in order to enhance equal distribution of copper throughout the soil. After liquid spiking silt was dried in the oven at 75°C and the big chunks were then ground by using a grinder in the Geotechnical lab. The ground silt was sieved using U.S.mesh. # 100 & 200 to remove the clay fraction. There is a possibility that $Cu(NO_3)_2$ might have been lost in the sieving process. Some studies have indicated that SFE of contaminants from soils containing higher clay contents are difficult (i.e. better extraction efficiencies are obtained for contaminants from a sandy soil than from a clay soil) (Hess *et al.*, 1991).

On the other hand results for the sand samples are quite different, although the spiking was done in the same way as for silt. After drying the Cu $(NO_3)_2$ crystals were still there and could be seen with the naked eye. This may explain why the concentration of Cu $(NO_3)_2$ in soil samples is sometimes higher and lower than the actual spiked concentration.

Visual observations of the solvent traps were also made. If only $Cu(tta)_2$ is present in the methanol traps, the methanol solutions be light green in colour. This however was not the case. During the extractions, the solvent traps were often light orange to bright orange in colour (see Table 4.4). According to Berg et al. (1960) and Satake et al. (1980), iron forms a red complex with tta, and therefore if iron is present in the soil, this complex may form. Both soils were therefore sent to Enviro-Test Labs for trace metal analysis using EPA Standard Method 6020. The results of this analysis are given in Table 4.3.

It is obvious from the analysis that a considerable amount of iron is present in the sand and silt. Due to the presence of other metals, there is a possibility that $Cu(tta)_2$ was not the only metal β-diketone present in the SC CO_2 stream flowing out of the vessel. Metal complexes other than $Cu(tta)_2$ like Fe, Co, Cr and Zn β-diketones may therefore have affected the copper extraction results because copper was not the only metal with which tta could complex. Mincher *et al.* (2001) noted that tta is not selective and may complex with many metals. Using a more selective chelating agent may increase copper extraction efficiency from the soil. Using tta in greater excess may also improve extraction efficiencies.

Table 4.3: Metal analysis for sand and silt from Enviro-Test

Metals	Concentration (mg/kg)		Detection limit
	Sand	silt	
Iron (Fe)	2800	18700	200
Silver (Ag)	<1	<1	1
Barium (Ba)	19	243	5
Beryllium (Be)	<1	<1	1
Cadmium (cd)	<0.5	0.5	0.5
Cobalt (Co)	1	8	1
Chromium (Cr)	1.7	13.5	0.5
Copper (Cu)	<2	19	2
Molybdenum (Mo)	<1	<1	1
Nickel (Ni)	3	21	2
Lead (Pb)	<5	10	5
Tin (Sn)	<5	<5	5
Strontium (Sr)	6	51	1
Thallium (Th)	<1	<1	1
Vanadium (V)	4	20	1
Zinc (Zn)	<10	70	10

Corrosion tests were performed in SC CO_2 to detect any corrosive attack on stainless steel during the metal extraction. Extraction was conducted by just putting tta in the extraction vessel to investigate if some of the iron is coming from corrosion of the stainless steel extraction system. Although the traps were not analyzed by ICP-MS, they were orange in color which indicates the presence of iron. The iron is therefore most likely originating from the stainless steel extraction vessel and tubing. It seems that corrosion is one of the main problems during the metal extraction and according to Ozel (2000) iron is the main component (66.7%) in stainless steel and it easily forms a complex with chelating agent. To minimize this problem, all stainless steel tubing downstream of the extraction vessel was replaced by PEEK tubing (99%, ACROS organics, Fisher Scientific, Nepean, ON). It should be noted that this tubing can only be operated reliably at a maximum temperature and pressure of 50°C and 20 MPa (Ozel *et al.,* 2000). These limited pressure and temperature ranges are undesirable as high supercritical fluid temperatures and pressures are known to increase analyte solubility and therefore extraction yields (Ozel *et al.,* 2000). Unfortunately the vessel could not be replaced by a PEEK vessel or by a vessel manufactured using some other inert material. Attempts were made to coat the vessel with Teflon™ or another inert material, but the problem was that a very thin coating was needed. The reason for thin coating was the small space between the mixer and the inner side of the vessel. The results didn't seem to be affected by just only replacing the stainless steel tubing by PEEK tubing.

4.4 EXTRACTION EFFICIENCY

After analyzing each soil sample for total copper concentration, extraction efficiencies was calculated for each extraction experiment. The extraction efficiency was calculated according to Equation 3.1 (see Section 3.2.7).

A sample calculation is presented in Appendix B3 and the extraction efficiencies for each experiment are given in the Table 4.4. Three sets of experiments were done at each condition of temperature and pressure except one in which a mixture of (tta + TBP + 10% H_2O) was used and the data presented in the table are the extraction experiments for which the extraction efficiencies are higher.

For each experiment, the soil was spiked with 80 mg Cu^{2+}/kg of soil. From the results one thing is clear that the extraction efficiency of sand increases from 36% to 56%

with the increase in pressure. In the literature pressures ranging from 10 MPa to 30 MPa and temperatures of 60°C have been considered to be optimal for the extraction of Cu^{+2} (Zhao *et al.*, 1999; Liu *et al.*, 2001). The extraction efficiencies do not appear to be influenced by the addition of a 1:1 mixture of tta and TBP or even the addition of 10% moisture. The use of a mixture of tta and TBP was recommended by Savoie (2002), and for this reason its effect was investigated. It is believed that TBP probably replaces the coordinated water molecules by forming adduct with the metal-β-diketone complexes, which become more soluble in supercritical CO_2 (Wai, 1996).

Table 4.4: Extraction efficiency of copper using SFE

Spiked Soil	Experiment	Ligand	P (MPa)	T (^oC)	M_b (µg of Cu/ kg soil)	M_a (µg of Cu/ kg soil)	EF (%)	Visual observations
Sand	1	tta	17.2	40	35.3	22.3	36.7	**Soil** = Sand after extraction was slightly red then before extraction **Trap color** = Traps were red and dark orange
	2	-	20.6	40	38.2	21.1	44.9	
	3	-	24.1	35	65.8	28.4	56.8	
	4	tta + TBP	24.1	35	39.1	28.6	26.9	
	5	tta + TBP +10%H_2O	24.1	35	36.0	31.7	11.9	
Silt	6	tta	17.2	40	117	108	8.0	**Soil** = There was no significant difference before and after the extraction **Trap color** = Traps were light orange
	7	-	20.6	40	58.4	53.8	7.8	
	8	-	24.1	35	45.4	44.4	2.0	
	9	tta + TBP	24.1	35	45.8	45.4	1.0	
	10	tta +TBP +10%H_2O	24.1	35	48.5	42.5	12.0	

% W (percent water) = 0, Ave = Average

TBP is neutral and cannot extract metals by SC CO_2 without counteranions. A mixture of tta and TBP appeared to extract more iron instead of copper because the traps were red and dark orange in color and may lead to the corrosion of the extraction vessel. According to Wai (1995), HFA combined with TBP can effectively extract metal ions from soil as compared to the extraction by tta and TBP, which is not very efficient. The presence of electron withdrawing fluorine in the ligands coordinated with the metal ions should enhance the Lewis acidity of the metal chelates, to form a more stable adducts with the Lewis base, TBP, and thus increases the solubility of metal chelates (Smart *et al.*, 1995).

The nature of solid matrix is also very important especially to determine the extraction efficiency of metal complexes by supercritical CO_2. When the solid surfaces are spiked with metal ions, their extraction efficiency should be higher then extraction efficiencies for metals from real soil, but this is not the case. The active sites and the natural ligands present in the real soil systems may bind strongly to certain metal ions hindering their complexation with added ligands (Wai *et al.*, 1997).

On the other hand the extraction efficiency of silt is low and the addition of (tta+TBP) alone has no effect. There is a slight increase in the extraction efficiency, when 10% water is added.

The water content in both the silt and the sand is almost zero that is why when water was added, the extraction efficiency of silt was increased. Wai *et al.* (1997) stated that the efficiency of metal extraction significantly increased when a small amount of water was added to a solid matrix such as filter paper, sand, soil or wood. The water presence may enhance the chelation of metals. Some studies have shown that water concentration in the range of 5 to 10 % increased the metal chelation of Pb, Zn, Cu and Co and yielded the highest extraction efficiencies of these metals from sand (Kersch *et al.*, 2000). According to Knipe *et al.* (1991), water may serve as a modifier for the solute/matrix interactions by blocking the active sites of the matrix and reducing the adsorption of the solute by the active sites of the polar matrix. Ozel *et al.* (1997) and Lin *et al.* (2003), suggest that water present at high levels may facilitate metal dissolution into the aqueous phase, its chelation (in part by deprotonating the chelating agent) and eventual extraction. Water has the ability to replace the metals and thus increase their migration from the matrix to the fluid phase. Moreover, water may also form adduct with the metal chelate, favoring its dissolution into the SCF (Ozel *et al.*, 1997). Two different moisture contents 5 % and 10 % were tested by Savoie (2002), but the optimum water content for silt and sand was not found. Therefore more extractions could be investigated at different water contents to find out the optimum moisture content for copper extraction from silt and sand.

4.5 MASS BALANCE RESULTS

The amount of copper in the traps can be determined by multiplying the volume of the traps by the concentration. These values are shown with the raw data in Appendix E. From these copper masses, the mass balance for the extraction experiments were calculated to ensure that all the copper placed inside the vessel could be accounted for. The mass balance results are presented in Table 4.5.

It is observed from the mass balance results that the amount of extracted Cu (in μg) is very low as compared to what was present in the spiked soil (i.e. 4000 μg of Cu). More experiments may be necessary to make more accurate calculations.

. **Table 4.5: Mass balance results of copper using SFE**

Spiked Soil	Ligand	P (MPa)	T (°C)	Mass Balance (μg of Cu^{+2})
Sand	tta	17.4	40	353
	-	20.6	40	454
	-	24.1	35	539
	tta + TBP	24.1	35	612
	tta + TBP +10%H_2O	24.1	35	679
Silt	tta	17.4	40	71
	-	20.6	40	99
	-	24.1	35	49
	tta + TBP	24.1	35	78
	tta + TBP +10%H_2O	24.1	35	255

4.6 SOLUBILITY ESTIMATION

The solubility of $Cu(tta)_2$ in SC CO_2 can be determined from the known concentration of $Cu(tta)_2$ in the solvent traps and the amount of CO_2 flowing through the trap. Sample calculations are given in Appendix F and data are summarized in Table 4.6.

From the Table 4.6, it can be seen from Experiment 1, 2 and 3 the solubility of Cu(tta)$_2$ increases with a rise in pressure. When a mixture of (tta+TBP) is added at 24.1 MPa and 35°C the solubility decreases which is probably due to the formation and dissolution of other metal complexes. As explained in Section 4.3.3, metal complexes other than Cu (tta)$_2$ may have effected the copper extraction results because it may have not the only metal present to complex with tta. Looking at Experiments 6 to 10, the solubility is higher for the experiment done with a mixture of (tta+TBP+10%w) at 24.1 MPa and 35°C.

Table 4.6: Solubility data for Cu(tta)$_2$ in SC CO$_2$

Spiked Soil	Experiment	Ligand	P (MPa)	T (°C)	Solubility (mol/ mol)
Sand	1	tta	17.4	40	2.89E -07
	2	-	20.6	40	3.09E -07
	3	-	24.1	35	3.13E -07
	4	tta + TBP	24.1	35	2.98E -07
	5	tta + TBP +10%H$_2$O	24.1	35	5.08E -07
Silt	6	tta	17.4	40	3.45E -08
	7	-	20.6	40	3.50E -08
	8	-	24.1	35	4.59E -09
	9	tta + TBP	24.1	35	1.46E -09
	10	tta + TBP +10%H$_2$O	24.1	35	1.58E -07

The solubilities found here are lower as compared to the previous work, where the average solubility was 1.41 x 10^{-6} mol/mol. The reason is the methodology used to determine the solubility of Cu(tta)$_2$. Previously solubility was determined directly by putting $Cu(tta)_2$ in the extraction vessel, but here in this project it was calculated for each extraction experiment from the amount of $Cu(tta)_2$ collected in the traps and the volume of CO_2 flowing through.

The cumulative mass of Cu^{+2} collected in the traps with respect to the cumulative mass of CO_2 is shown in Figure 4.12 and the data is given in Appendix G. It can be seen that the cumulative mass of Cu^{+2} increases with respect to the cumulative mass of CO_2.

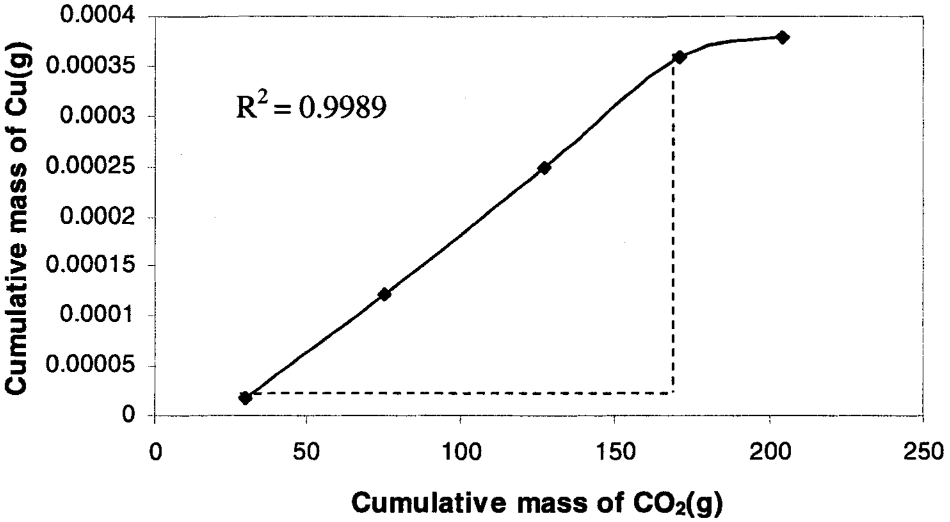


Figure 4.12: Cumulative mass of Cu (g) vs Cumulative mass of CO_2 (g) during SC CO_2 extractions for spiked sand soil at 35^0C and 24.1 MPa

It would therefore, appear that the extractions and the extraction efficiencies are limited by the amount of metal chelates that can dissolve into a certain amount of CO_2, i.e. the solubility of $Cu(tta)_2$ in SC CO_2.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

Extractions experiments were conducted to extract copper from spiked soil using thenoyltrifluoroacetone as a chelating agent. Two types of soil were used in this research work, silt and sand. Extractions were carried out at different conditions of temperature and pressure and details are given in Chapter 3. Some of the experiments were performed using a mixture of thenoyltrifluoroacetone and tributylphosphate. For each soil one extraction is carried out by adding 10% water.

The results suggests that appreciable amount of copper is extracted from sand at 24.1 MPa and 35°C. The extraction efficiency seems to increase from 36 % to 56 % for the sand. TBP was expected to increase the extraction efficiency, but no increase was observed. The extraction of copper from the silt was challenging and for this reason, different conditions were applied. It seemed that the addition of 10 % water improve the extraction of copper the silt. Due to limited time different water contents were not tested in order to determine a optimum water content.

In order to achieve higher extraction efficiencies, some changes were made to the SFE setup. Stainless steel tubing was replaced by PEEK tubing to minimize the corrosion, which was the main problem during the copper extractions. Based on visual observations it appeared that other metals were being extracted by the tta. Extraction of other metals (other then Cu^{+2}) may have lead to the low extraction efficiencies observed in this work. Adding more tta (in excess) or using a more selective complexing agent than tta may improve Cu^{+2} extraction by SC CO_2.

5.1 RECOMMENDATIONS

SC CO_2 Extractions

- Further study would be needed to determine an appropriate material that can be used to coat the vessel in order to minimize any corrosion.

- Experiments should be carried out at higher temperatures and pressures and at different water contents. These conditions should be better optimized until acceptable extraction efficiencies can be obtained.

- More experiments need to be done using other chelating agents (more selective chelating agents) at the same experimental conditions of temperature and pressure to compare the extraction efficiencies.

- A combination of tributylphosphate (TBP) and other β-diketones should be tested to observe a synergistic extraction of the metal in question which may yield better extraction efficiencies than the present one.

CHAPTER 6 REFERENCES

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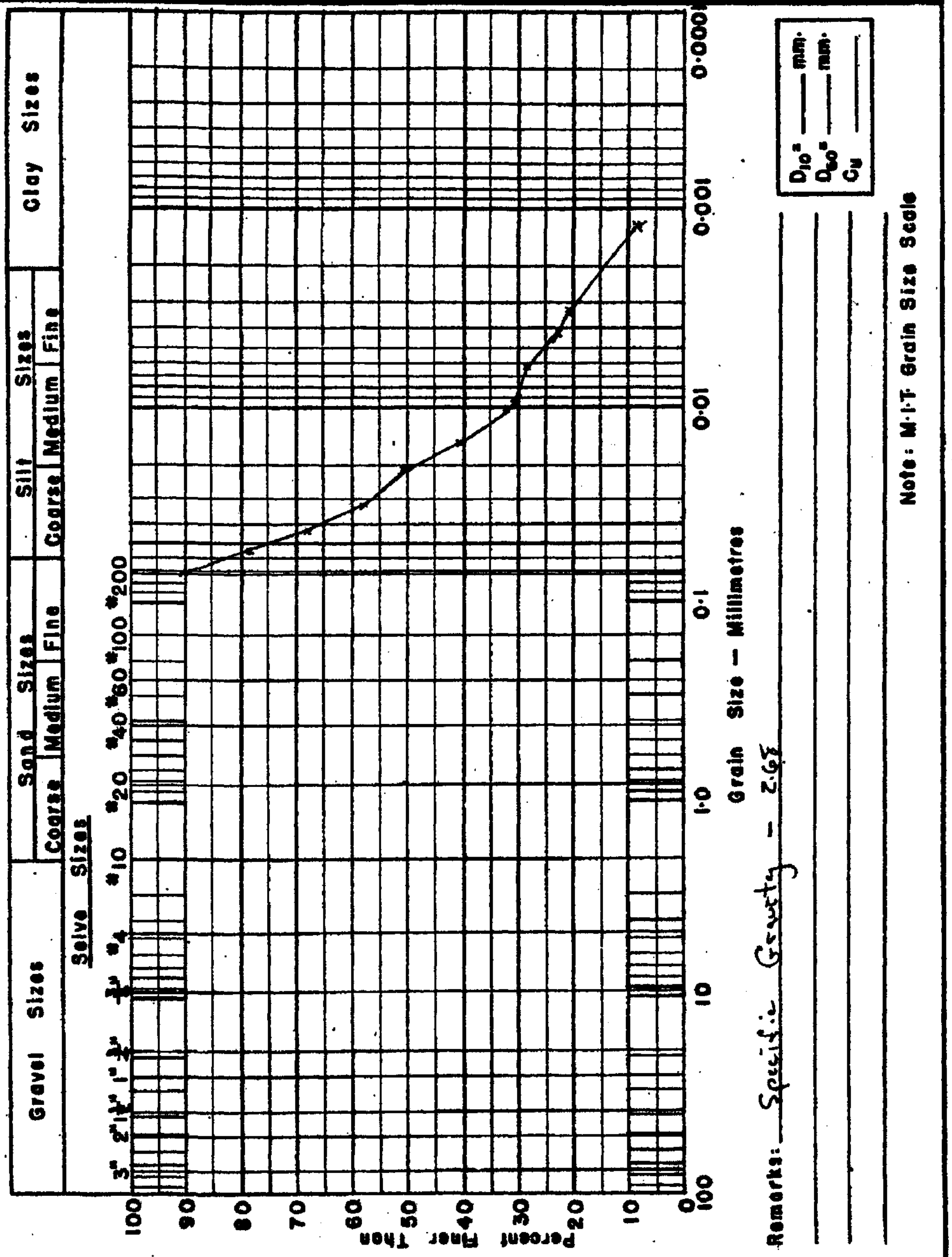
APPENDIX A

UNIVERSITY of ALBERTA
DEPT of CIVIL ENGINEERING
SOIL MECHANICS LABORATORY

GRAIN SIZE CURVE

PROJECT Teaching Labs	
SITE Test Site J Ground	
SAMPLE Devon Silt	
LOCATION Devon	
HOLE	DEPTH
TECHNICIAN	DATE



Remarks: Specific Gravity – 2.65

APPENDIX B

APPENDIX B1: Sample Calculations for External and Internal standards

Copper standard of concentration 1000 mg/L was used as an external standard in ICP-MS calibration. The concentration is high enough, so 1 ppm working standard was prepared from copper stock solution of concentration 1000 mg.L^{-1} (99%, ACROS organics, Fisher Scientific, Nepean, ON). Then 1 ppm working standard was used to make further dilution of 2ppb, 10pbb, 50ppb, and 100ppb.

To make 1 ppm working solution (in 10mL) from 1000 ppm stock solution,

$$1000 \text{ ppm} * ? \text{ mL} = 1 \text{ ppm} * 10 \text{ mL}$$

So, 0.01 mL in 10 mL

Or 10 uL in 10 mL

To make 2 ppb or 0.002 ppm (in 50 mL) from the above 1 ppm working solution,

$$1 \text{ ppm} * ? \text{ mL} = 0.002 \text{ ppm} * 50 \text{ mL}$$

So, we need 0.1 mL in 50 mL
or 1 uL

Ge (10 mg/ L) (99%, ACROS organics, Fisher Scientific, Nepean, ON) was used as an internal standard in Samlpes, standards and blanks.

To make 50 ppb or 0.05 ppm we need,

$$0.05 * 50 \text{ mL} = ? \text{ mL} * 10 \text{ ppm}$$

0.25 mL or 250 uL

APPENDIX B2: Sample Calculations for the solvent traps and the soil

(i) Solvent traps

For each extraction 50g of soil was taken. The soil (sand or silt) was spiked with 80mg Cu/Kg of soil. It is important to calculate the concentration of Cu in 50g of soil in order to do the mass balance.

50g of soil spiked with 80 mg Cu/Kg of soil

So,

50g * 80mg/Kg = 4mg or 4000ug

This means that 50g of soil contain 4000ug of Cu.

(ii) Soil

In order to analyze the soil samples by ICP-MS, it is necessary to perform acid digestion. For acid digestion 0.5g of soil was taken in 10 mL of HNO_3. The soil (sand or silt) was spiked with 80mg Cu/Kg of soil.

0.5g of soil spiked with 80 mg Cu/Kg of soil

So,

0.5g * 80mg/Kg = 0.04mg or 40ug

This means that 0.5g of soil contain 40ug of Cu.

APPENDIX B3: Sample Calculations for the Extraction efficiency

The extraction efficiency can be calculated from the mass of the Copper measured by the ICP-MS. The equation used to calculate the extraction efficiency is given below in eq. A2.

$$\mathrm{EF\%} = \frac{Mb - Ma}{Mb} \times 100 \qquad \text{(A2)}$$

Where,

Mb = mass before the extraction

Ma = mass after the extraction

For the extraction of spiked sand 2005-09-28 @ 3500Psi and 35°C

$Mb = 65.80$

$Ma = 28.42$

$$\mathrm{EF\%} = \frac{65.80 - 28.42}{65.80} \times 100$$

$$\mathrm{EF\%} = 56.82\%$$

APPENDIX C

Appendix C: Sample spreadsheet of SC CO_2 extraction experiment data

Date: 2005-09-09

Filename: 2005-09-09 at 20.7 MPa and 40°C

Comments: 50 g of spiked soil at 20.7 MPa and 40°C in the vessel. Pump A and Pump B already refilled and pressurized to 20.7 MPa. Pump B opened to the vessel at 61s. Static period started at 281s and ends at 3601s, when dynamic period started at 3621s. The dynamic period ends at 8121s and Lab View stopped at 8871s.

Time	Pump pressure (MPa)			Pressure	Pump Flow (mL/min)			Temperature
(s)	Pump A	Pump B	Total	Transducer	Pump A	Pump B	Total	(°C)
				(MPa)				
Start of run. Lab View data acquisition started, both pumps already pressurized to 20.7MPa but not open to the vessel yet.								
11	19.5	19.5	19.5	0.67	15.6	16.6	0.0	25.4
20	19.4	19.4	19.4	7.7	96.1	97.1	0.0	31.2
31	20.4	20.4	20.4	8.1	87.9	88.9	0.0	33.6
41	20.4	20.4	20.4	8.8	22.9	23.9	0.0	33.4
50	20.3	20.3	20.3	9.3	19.1	20.1	0.0	31.0
Pressurized flow opened to the vessel at 61s.								
61	20.3	20.3	20.3	9.9	11.3	12.3	0.0	33.9
71	20.3	20.3	20.3	11.2	-0.2	0.8	0.0	36.7
81	20.7	20.7	20.7	13.9	0.6	1.6	0.0	39.7
90	20.8	20.8	20.8	18.2	0.7	1.7	0.0	42.1
101	20.8	20.8	20.8	21.1	0.7	1.7	0.0	42.9
111	20.7	20.7	20.7	21.3	0.8	1.8	0.0	42.2
120	20.7	20.7	20.7	21.3	0.7	1.7	0.0	41.4
131	20.7	20.7	20.7	21.3	0.8	1.8	0.0	40.9
141	20.7	20.7	20.7	21.3	0.7	1.7	0.0	40.6
150	20.7	20.7	20.7	21.1	0.8	1.8	0.0	40.3
161	20.7	20.7	20.7	21.3	0.8	1.8	0.0	40.0
170	20.7	20.7	20.7	21.3	0.7	1.7	0.0	40.0
180	20.7	20.7	20.7	21.3	0.7	1.7	0.0	40.0
191	20.7	20.7	20.7	21.4	0.7	1.7	0.0	40.0
200	20.7	20.7	20.7	21.3	0.7	1.7	0.0	39.9
210	20.7	20.7	20.7	21.3	0.7	1.7	0.0	39.9

221	20.7	20.7	20.7	21.3	0.7	1.7	0.0	39.9
230	20.7	20.7	20.7	21.3	0.7	1.7	0.0	39.7
240	20.7	20.7	20.7	21.3	0.7	1.7	0.0	39.9
251	20.7	20.7	20.7	21.3	0.6	1.6	0.0	40.0
261	20.7	20.7	20.7	21.3	0.6	1.6	0.0	39.9
270	20.7	20.7	20.7	21.4	0.6	1.6	0.0	40.0
Static period started at 281s								
281	20.7	20.7	20.7	21.3	0.6	1.6	0.0	40.0
290	20.7	20.7	20.7	21.4	0.6	1.6	0.0	40.0
300	20.7	20.7	20.7	21.4	0.6	1.6	0.0	40.1
311	20.7	20.7	20.7	21.3	0.6	1.6	0.0	40.1
320	20.7	20.7	20.7	21.4	0.6	1.6	0.0	40.1
330	20.7	20.7	20.7	21.4	0.6	1.6	0.0	40.2
341	20.7	20.7	20.7	21.4	0.6	1.6	0.0	40.2
350	20.7	20.7	20.7	21.3	0.5	1.5	0.0	40.2
360	20.7	20.7	20.7	21.3	0.5	1.5	0.0	40.3
371	20.7	20.7	20.7	21.4	0.5	1.5	0.0	40.3
380	20.7	20.7	20.7	21.4	0.5	1.5	0.0	40.3
390	20.7	20.7	20.7	21.4	0.5	1.5	0.0	40.4
401	20.7	20.7	20.7	21.3	0.5	1.5	0.0	40.4
410	20.7	20.7	20.7	21.4	0.5	1.5	0.0	40.4
420	20.7	20.7	20.7	21.4	0.5	1.5	0.0	40.5
431	20.7	20.7	20.7	21.4	0.5	1.5	0.0	40.5
440	20.7	20.7	20.7	21.4	0.5	1.5	0.0	40.5
450	20.7	20.7	20.7	21.3	0.5	1.5	0.0	40.5
461	20.7	20.7	20.7	21.3	0.4	1.4	0.0	40.5
470	20.7	20.7	20.7	21.4	0.5	1.5	0.0	40.6
480	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.6
491	20.7	20.7	20.7	21.3	0.4	1.4	0.0	40.6
500	20.7	20.7	20.7	21.3	0.4	1.4	0.0	40.6
510	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.6
521	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.6
530	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.6
540	20.7	20.7	20.7	21.3	0.4	1.4	0.0	40.6
551	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.6
560	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.6
570	20.7	20.7	20.7	21.3	0.4	1.4	0.0	40.7
581	20.7	20.7	20.7	21.3	0.4	1.4	0.0	40.7
590	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.7
600	20.7	20.7	20.7	21.3	0.4	1.4	0.0	40.7
611	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.6
620	20.7	20.7	20.7	21.4	0.4	1.4	0.0	40.7
631	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.7
641	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.8
650	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.8
660	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.7
671	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.8

681	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.7
690	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.8
701	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.8
711	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
720	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.8
731	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.7
741	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.8
750	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
761	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.9
771	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.8
780	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.9
791	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
801	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.9
810	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
821	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
831	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.8
840	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
851	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
861	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
870	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
881	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
891	20.7	20.7	20.7	21.3	0.3	1.3	0.0	40.9
900	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9
911	20.7	20.7	20.7	21.4	0.3	1.3	0.0	40.9
921	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
930	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
941	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
951	20.7	20.7	20.7	21.1	0.2	1.2	0.0	40.9
960	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9
971	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9
981	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
990	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
1001	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9
1011	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
1020	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9
1031	20.7	20.7	20.7	21.2	0.2	1.2	0.0	40.8
1041	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
1050	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
1061	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9
1071	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
1080	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.8
1091	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9
1101	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.9
1110	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.8
1121	20.7	20.7	20.7	21.3	0.2	1.2	0.0	40.8
1131	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.7
1140	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9
1151	20.7	20.7	20.7	21.4	0.2	1.2	0.0	40.9

1161	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.1
1170	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.2
1181	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.2
1191	20.7	20.7	20.7	21.3	0.2	1.2	0.0	41.1
1200	20.7	20.7	20.7	21.3	0.2	1.2	0.0	41.1
1211	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.1
1221	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.2
1230	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.2
1241	20.7	20.7	20.7	21.3	0.2	1.2	0.0	41.4
1251	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.4
1260	20.7	20.7	20.7	21.3	0.2	1.2	0.0	41.3
1270	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.2
1281	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.2
1290	20.7	20.7	20.7	21.2	0.2	1.2	0.0	41.3
1300	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1311	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1320	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1330	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.4
1341	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.3
1350	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.3
1360	20.7	20.7	20.7	21.3	0.2	1.2	0.0	41.5
1371	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1380	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1390	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1401	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1410	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.4
1421	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1431	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.6
1440	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.6
1451	20.7	20.7	20.7	21.3	0.2	1.2	0.0	41.6
1461	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.6
1470	20.7	20.7	20.7	21.4	0.2	1.2	0.0	41.5
1481	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.5
1491	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1500	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1510	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1521	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.6
1530	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.6
1540	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.5
1551	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.6
1560	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1570	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1581	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1591	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1600	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.6
1611	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.6
1621	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1630	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8

1641	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1651	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.8
1660	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1671	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1681	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1690	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1701	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1711	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1720	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1731	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1741	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.7
1750	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1761	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1771	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1780	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1791	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1801	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1810	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1821	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1831	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1840	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1851	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1861	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1870	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1881	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.7
1891	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1900	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1911	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
1921	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1930	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1941	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1951	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1960	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
1971	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
1981	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
1990	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.8
2001	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2011	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2020	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.8
2031	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2041	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2050	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2061	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2071	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2080	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2091	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2101	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2110	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0

2121	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2131	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2140	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2151	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2161	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2170	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2181	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2191	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2200	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2211	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2221	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2230	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2241	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2251	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2260	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2271	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2281	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2290	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.8
2301	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2311	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2320	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2331	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2341	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2350	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.9
2361	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.8
2371	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2380	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2391	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2401	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2410	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2421	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2431	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2440	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2451	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2461	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2470	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.0
2481	20.7	20.7	20.7	21.3	0.2	1.2	0.0	42.1
2491	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2500	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2511	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2521	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2530	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2541	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2551	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2560	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2571	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2581	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2590	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9

2601	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2611	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2620	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2631	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2641	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.8
2650	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2661	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2671	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2680	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.0
2691	20.7	20.7	20.7	21.2	0.1	1.1	0.0	42.0
2701	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2710	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2721	20.7	20.7	20.7	21.2	0.1	1.1	0.0	41.8
2731	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2740	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2751	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2761	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2770	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2780	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2791	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2800	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2811	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2821	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
2830	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2841	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2851	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2860	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2871	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2881	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2890	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2901	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2911	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2920	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2931	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
2941	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2950	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
2961	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
2971	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
2980	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
2991	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
3001	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3010	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
3021	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3031	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3040	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3051	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3061	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
3070	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9

3081	20.7	20.7	20.7	21.4	0.0	1.0	0.0	42.2
3091	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3100	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3111	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3121	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3130	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
3141	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3151	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3160	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3171	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3181	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3190	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3201	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
3211	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3220	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3231	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3241	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3250	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
3261	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3271	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3280	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
3291	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3301	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3310	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3321	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3331	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3340	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
3351	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3361	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3370	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3381	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3391	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3400	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3411	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3421	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3430	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3441	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3451	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3460	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
3471	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3481	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.0
3490	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3501	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3511	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3520	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3531	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3541	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3550	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1

3561	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3571	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3580	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3591	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3601	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3610	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
Dynamic period started at 3621s								
3621	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
3631	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3640	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3651	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3661	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3670	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3681	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3691	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3700	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3711	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3721	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3730	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3741	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
3751	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3760	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3771	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3781	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3790	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3801	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3811	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3820	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
3831	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3841	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3850	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3861	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.3
3871	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
3880	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3891	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3901	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
3910	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
3921	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3931	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3940	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
3951	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.3
3961	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
3970	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
3981	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
3991	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
4000	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.3
4011	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2

4021	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
4030	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
4041	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
4051	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4060	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4071	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4081	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4090	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4101	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
4111	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4120	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4131	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4141	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.3
4150	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4161	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4171	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4180	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.3
4191	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.3
4201	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.3
4210	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4221	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4231	20.7	20.7	20.7	21.1	0.1	1.1	0.0	42.2
4240	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4251	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4261	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4270	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4281	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4291	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4300	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4311	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4321	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4330	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4341	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4351	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4360	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4371	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4381	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4390	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4401	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4411	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4420	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
4431	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4441	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4450	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4461	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
4471	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4480	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4491	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2

4501	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4510	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4521	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4531	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4540	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4551	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4561	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4570	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4581	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4591	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
4600	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4611	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4620	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4630	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4641	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4650	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
4660	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4671	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4681	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4690	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4701	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4711	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4720	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
4731	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4741	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4750	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4761	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
4771	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4780	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.2
4791	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4800	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4810	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4821	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4830	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.0
4840	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
4851	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4860	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
4870	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4881	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4890	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.0
4900	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4911	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4920	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4930	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4941	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
4950	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9
4960	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
4971	20.7	20.7	20.7	21.4	0.1	1.1	0.0	41.9

4980	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.0
4990	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
5001	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
5010	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
5020	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.1
5031	20.7	20.7	20.7	21.3	0.1	1.1	0.0	41.9
5040	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
5050	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.0
5061	20.7	20.7	20.7	21.3	0.1	1.1	0.0	42.1
5070	20.7	20.7	20.7	21.4	0.1	1.1	0.0	42.2
5080	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5091	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5100	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5110	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5121	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5130	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5140	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5151	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5160	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5170	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5181	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5190	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5200	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5211	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5220	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5230	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5241	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5250	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5261	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
5271	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
5280	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5290	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5301	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5310	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5320	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5331	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5340	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5350	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5361	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5370	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5380	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5391	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5400	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5411	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5421	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5430	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5441	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5451	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9

5460	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5471	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5481	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.6
5490	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5501	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5511	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5521	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5530	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5541	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5550	20.7	20.7	20.7	21.1	0.1	1.1	0.0	40.7
5560	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
5571	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5580	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5590	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5601	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5610	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5620	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5631	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5640	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5650	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5661	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5670	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5680	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5691	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5700	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5710	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5721	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5730	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5740	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5751	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5760	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5770	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5781	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5790	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5800	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5811	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5820	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5830	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5841	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5850	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5860	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5871	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5880	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5890	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5901	20.7	20.7	20.7	21.1	0.1	1.1	0.0	40.8
5910	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
5920	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
5931	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8

5940	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5950	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5961	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
5970	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
5980	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
5991	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6000	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6010	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6021	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6030	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6041	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6051	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6060	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6071	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.6
6081	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6090	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6101	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6111	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6120	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6130	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6141	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
6150	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6160	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6171	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6180	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6191	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6201	20.7	20.7	20.7	21.3	0.0	1.0	0.0	40.7
6210	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6221	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6231	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6240	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6250	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6261	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6270	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6280	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6291	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6300	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6310	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6321	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6330	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6340	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6351	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
6360	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6370	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6381	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6390	20.7	20.7	20.7	21.2	0.0	1.0	0.0	40.9
6400	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6411	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9

6420	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6430	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6441	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6450	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6460	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6471	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6481	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6490	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6501	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6511	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.6
6520	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6531	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6541	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6550	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6561	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6571	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6580	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.6
6591	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6601	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6610	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6621	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6630	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6640	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6651	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6660	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.6
6670	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6681	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6691	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6700	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6711	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6721	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
6730	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6741	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6751	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6760	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6771	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6780	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6790	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6801	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.6
6810	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6820	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6831	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6840	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6850	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6861	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6870	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
6880	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
6891	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8

6900	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6910	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
6921	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6930	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6940	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
6951	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6960	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
6970	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
6981	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
6990	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
7000	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
7011	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
7020	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
7030	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.6
7041	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
7050	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7060	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7071	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9
7080	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
7090	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
7101	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
7110	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
7120	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7131	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7140	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7150	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7161	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
7170	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
7180	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.6
7191	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
7200	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
7210	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
Dynamic period ends at 7221s and bypass is started								
7221	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7230	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
7240	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
7251	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
7260	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
7271	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
7281	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7290	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7300	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
7311	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
7320	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.7
7330	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.6
7341	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.8
7350	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.9

7360	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.9
7371	20.7	20.7	20.7	21.3	0.1	1.1	0.0	40.8
7380	20.7	20.7	20.7	21.2	0.1	1.1	0.0	40.7
7390	20.6	20.6	20.6	21.2	0.1	1.1	0.0	40.8
7401	20.3	20.3	20.3	21.2	3.1	4.1	0.0	40.6
7410	20.4	20.4	20.4	21.2	2.4	3.4	0.0	40.7
7421	20.4	20.4	20.4	21.2	2.5	3.5	0.0	40.9
7431	20.4	20.4	20.4	21.2	2.5	3.5	0.0	40.9
7440	20.4	20.4	20.4	21.2	2.2	3.2	0.0	40.9
7451	20.4	20.4	20.4	21.1	2.2	3.2	0.0	40.8
7461	20.4	20.4	20.4	21.1	2.2	3.2	0.0	40.6
7470	20.4	20.4	20.4	21.1	2.2	3.2	0.0	40.7
7481	20.3	20.3	20.3	21.1	1.8	2.8	0.0	40.8
7491	20.3	20.3	20.3	21.1	2.6	3.6	0.0	40.9
7500	20.3	20.3	20.3	21.1	2.3	3.3	0.0	40.9
7511	20.3	20.3	20.3	21.1	2.2	3.2	0.0	40.9
7521	20.4	20.4	20.4	21.0	2.2	3.2	0.0	40.8
7530	20.4	20.4	20.4	20.9	2.1	3.1	0.0	40.7
7541	20.4	20.4	20.4	20.9	2.1	3.1	0.0	40.7
7551	20.4	20.4	20.4	21.0	2.3	3.3	0.0	40.8
7560	20.3	20.3	20.3	20.8	2.2	3.2	0.0	40.9
7571	20.3	20.3	20.3	21.0	2.0	3.0	0.0	40.9
7581	20.4	20.4	20.4	21.0	1.8	2.8	0.0	40.9
7590	20.4	20.4	20.4	20.9	1.7	2.7	0.0	40.8
7601	20.4	20.4	20.4	20.9	1.7	2.7	0.0	40.7
7611	20.3	20.3	20.3	20.8	1.8	2.8	0.0	40.6
7620	20.3	20.3	20.3	20.9	1.9	2.9	0.0	40.9
7631	20.3	20.3	20.3	20.9	1.8	2.8	0.0	40.9
7641	20.3	20.3	20.3	20.9	1.5	2.5	0.0	40.9
7650	20.4	20.4	20.4	20.8	1.5	2.5	0.0	40.9
7661	20.3	20.3	20.3	20.8	1.6	2.6	0.0	40.8
7671	20.3	20.3	20.3	20.8	1.5	2.5	0.0	40.8
7680	20.3	20.3	20.3	20.8	1.6	2.6	0.0	40.7
7691	20.3	20.3	20.3	20.9	1.7	2.7	0.0	40.9
7701	20.3	20.3	20.3	20.8	1.4	2.4	0.0	40.9
7710	20.3	20.3	20.3	20.8	1.3	2.3	0.0	40.9
7721	20.3	20.3	20.3	20.8	1.3	2.3	0.0	40.9
7731	20.4	20.4	20.4	20.8	1.2	2.2	0.0	40.9
7740	20.4	20.4	20.4	20.7	1.3	2.3	0.0	40.8
7751	20.4	20.4	20.4	20.7	1.4	2.4	0.0	40.7
7761	20.3	20.3	20.3	20.8	1.4	2.4	0.0	40.9
7770	20.3	20.3	20.3	20.8	1.1	2.1	0.0	40.9
7781	20.4	20.4	20.4	20.8	1.1	2.1	0.0	40.9
7791	20.4	20.4	20.4	20.7	1.1	2.1	0.0	40.9
7800	20.4	20.4	20.4	20.7	1.1	2.1	0.0	40.9
7811	20.4	20.4	20.4	20.7	1.2	2.2	0.0	40.8
7821	20.3	20.3	20.3	20.7	1.3	2.3	0.0	40.7
7830	20.3	20.3	20.3	20.8	1.1	2.1	0.0	40.9

7841	20.4	20.4	20.4	20.8	1.0	2.0	0.0	40.9
7851	20.4	20.4	20.4	20.7	1.0	2.0	0.0	41.0
7860	20.4	20.4	20.4	20.7	1.0	2.0	0.0	41.0
7871	20.4	20.4	20.4	20.7	1.0	2.0	0.0	40.9
7881	20.4	20.4	20.4	20.6	1.2	2.2	0.0	40.8
7890	20.3	20.3	20.3	20.7	1.2	2.2	0.0	40.8
7901	20.4	20.4	20.4	20.7	1.0	2.0	0.0	40.9
7911	20.4	20.4	20.4	20.7	0.9	1.9	0.0	40.9
7920	20.4	20.4	20.4	20.7	0.9	1.9	0.0	41.0
7931	20.4	20.4	20.4	20.7	0.9	1.9	0.0	40.9
7941	20.4	20.4	20.4	20.7	1.0	2.0	0.0	40.9
7950	20.4	20.4	20.4	20.5	1.2	2.2	0.0	40.8
7961	20.4	20.4	20.4	20.6	1.1	2.1	0.0	40.9
7971	20.4	20.4	20.4	20.7	0.8	1.8	0.0	40.9
7980	20.4	20.4	20.4	20.6	0.9	1.9	0.0	41.0
7991	20.4	20.4	20.4	20.7	0.9	1.9	0.0	41.0
8001	20.4	20.4	20.4	20.5	0.9	1.9	0.0	41.0
8010	20.4	20.4	20.4	20.6	1.0	2.0	0.0	40.9
8021	20.4	20.4	20.4	20.5	1.1	2.1	0.0	40.8
8031	20.4	20.4	20.4	20.5	0.9	1.9	0.0	40.8
8040	20.4	20.4	20.4	20.5	0.8	1.8	0.0	40.9
8051	20.4	20.4	20.4	20.6	0.8	1.8	0.0	40.9
8061	20.4	20.4	20.4	20.6	0.8	1.8	0.0	41.0
8070	20.3	20.3	20.3	20.6	1.0	2.0	0.0	40.9
8081	20.4	20.4	20.4	20.5	1.0	2.0	0.0	40.9
8091	20.4	20.4	20.4	20.4	1.0	2.0	0.0	40.8
8100	20.4	20.4	20.4	20.4	0.7	1.7	0.0	40.9
8111	20.4	20.4	20.4	20.4	0.7	1.7	0.0	40.8
8121	20.4	20.4	20.4	20.5	0.7	1.7	0.0	40.9
8130	20.4	20.4	20.4	20.5	0.8	1.8	0.0	40.9
8141	20.4	20.4	20.4	20.5	0.8	1.8	0.0	40.9
8151	20.4	20.4	20.4	20.5	1.0	2.0	0.0	41.0
8160	20.4	20.4	20.4	20.4	0.7	1.7	0.0	40.9
8171	20.4	20.4	20.4	20.4	0.7	1.7	0.0	40.8
8181	20.4	20.4	20.4	20.4	0.7	1.7	0.0	40.8
8190	20.4	20.4	20.4	20.4	0.7	1.7	0.0	40.9
8201	20.4	20.4	20.4	20.5	0.7	1.7	0.0	40.9
8211	20.4	20.4	20.4	20.5	0.8	1.8	0.0	41.0
8220	20.4	20.4	20.4	20.5	0.8	1.8	0.0	41.0
8231	20.4	20.4	20.4	20.4	0.7	1.7	0.0	40.9
8241	20.4	20.4	20.4	20.4	0.6	1.6	0.0	40.9
8250	20.4	20.4	20.4	20.3	0.6	1.6	0.0	40.9
8261	20.4	20.4	20.4	20.4	0.6	1.6	0.0	40.9
8271	20.4	20.4	20.4	20.4	0.7	1.7	0.0	41.0
8280	20.4	20.4	20.4	20.4	0.8	1.8	0.0	41.0
8291	20.4	20.4	20.4	20.5	0.1	1.1	0.0	41.0
8301	20.4	20.4	20.4	20.2	0.2	1.2	0.0	40.9
8310	20.4	20.4	20.4	20.3	0.1	1.1	0.0	40.9

8321	20.4	20.4	20.4	20.2	0.1	1.1	0.0	40.8
8331	20.4	20.4	20.4	20.2	0.1	1.1	0.0	40.6
8340	20.4	20.4	20.4	20.2	0.1	1.1	0.0	40.6
8351	20.3	20.3	20.3	20.1	0.0	1.0	0.0	40.5
8361	20.3	20.3	20.3	20.2	0.0	1.0	0.0	40.4
8370	20.3	20.3	20.3	20.1	0.0	1.0	0.0	40.4
8381	20.3	20.3	20.3	20.1	0.0	1.0	0.0	40.4
8391	20.3	20.3	20.3	20.1	0.0	1.0	0.0	40.3
8400	20.3	20.3	20.3	20.0	0.0	1.0	0.0	40.3
8411	20.3	20.3	20.3	20.0	0.0	1.0	0.0	40.2
8421	20.3	20.3	20.3	13.5	0.0	1.0	0.0	37.2
8430	20.3	20.3	20.3	11.5	0.0	1.0	0.0	34.2
8441	20.3	20.3	20.3	10.6	0.0	1.0	0.0	33.4
8451	20.3	20.3	20.3	9.9	0.0	1.0	0.0	33.4
8460	20.3	20.3	20.3	9.6	0.0	1.0	0.0	33.5
8471	20.3	20.3	20.3	9.4	0.0	1.0	0.0	33.7
8481	20.3	20.3	20.3	9.2	0.0	1.0	0.0	33.9
8490	20.3	20.3	20.3	9.1	0.0	1.0	0.0	34.0
8501	20.3	20.3	20.3	8.9	0.0	1.0	0.0	34.2
8511	20.3	20.3	20.3	9.0	0.0	1.0	0.0	34.4
8520	20.3	20.3	20.3	8.9	0.0	1.0	0.0	34.5
8531	20.3	20.3	20.3	8.8	0.0	1.0	0.0	34.5
8541	20.3	20.3	20.3	8.6	0.0	1.0	0.0	34.0
8550	20.3	20.3	20.3	8.6	0.0	1.0	0.0	33.9
8561	20.3	20.3	20.3	8.6	0.0	1.0	0.0	33.9
8571	20.3	20.3	20.3	8.5	0.0	1.0	0.0	34.0
8580	20.3	20.3	20.3	8.5	0.0	1.0	0.0	34.0
8591	20.3	20.3	20.3	8.4	0.0	1.0	0.0	33.8
8601	20.3	20.3	20.3	8.4	0.0	1.0	0.0	33.6
8610	20.3	20.3	20.3	8.4	0.0	1.0	0.0	33.4
8621	20.3	20.3	20.3	8.2	0.0	1.0	0.0	33.1
8631	20.3	20.3	20.3	8.1	0.0	1.0	0.0	32.8
8640	20.2	20.2	20.2	8.0	0.0	1.0	0.0	32.4
8651	20.3	20.3	20.3	7.9	0.0	1.0	0.0	31.4
8661	20.3	20.3	20.3	7.8	0.0	1.0	0.0	30.8
8670	20.3	20.3	20.3	7.6	0.0	1.0	0.0	30.1
8681	20.3	20.3	20.3	7.5	0.0	1.0	0.0	29.4
8691	20.3	20.3	20.3	7.3	0.0	1.0	0.0	28.7
8700	20.3	20.3	20.3	7.2	0.0	1.0	0.0	28.2
8711	20.3	20.3	20.3	7.1	0.0	1.0	0.0	27.5
8721	20.3	20.3	20.3	6.9	0.0	1.0	0.0	27.0
8730	20.3	20.3	20.3	6.4	0.0	1.0	0.0	26.6
8741	20.3	20.3	20.3	5.4	0.0	1.0	0.0	22.6
8751	20.3	20.3	20.3	4.3	0.0	1.0	0.0	18.0
8760	20.3	20.3	20.3	4.0	0.0	1.0	0.0	15.4
8771	20.3	20.3	20.3	3.1	0.0	1.0	0.0	14.7
8781	20.3	20.3	20.3	2.8	0.0	1.0	0.0	15.0
8790	20.3	20.3	20.3	2.4	0.0	1.0	0.0	15.7

8801	20.3	20.3	20.3	1.7	0.0	1.0	0.0	15.9
8811	20.3	20.3	20.3	1.3	0.0	1.0	0.0	15.5
8820	20.4	20.4	20.4	1.1	0.0	1.0	0.0	15.4
8831	20.4	20.4	20.4	0.9	0.0	1.0	0.0	15.6
8841	20.4	20.4	20.4	0.6	0.0	1.0	0.0	16.0
8850	20.4	20.4	20.4	0.7	0.0	1.0	0.0	16.5
8861	20.4	20.4	20.4	0.4	0.0	1.0	0.0	17.2
8871	20.4	20.4	20.4	0.6	0.0	1.0	0.0	18.0
Lab View data acquisition stopped								

APPENDIX D

Appendix D: Results of Solvent traps analyzed by ICP-MS

Table D-1: Spiked Silt - 16-08-2005 @ 40oC and 17.2 MPa

Mass of Cu (ug)	CO2 flowed (L)	Cu(ug)/L of CO2	Time
1.69	8.04	0.21	15
0.92	7.14	0.13	30
0.84	9	0.09	45
1.37	7.23	0.19	60
0.68	10.46	0.06	75

Table D -2: Spiked Silt - 13-09-2005 @ 40oC and 20.7 MPa

Mass of Cu (ug)	CO2 flowed (L)	Cu(ug)/L of CO2	Time
14.64	10.11	1.448	15
10.62	7.73	1.374	30
10.81	11.75	0.920	45
10.43	11.11	0.939	60
3.23	8.86	0.364	75

Table D-3: Spiked Silt - 05-10-2005 @ 35oC and 24.1 MPa

Mass of Cu (ug)	CO2 flowed (L)	Cu(ug)/L of CO2	Time
1.07	5.65	0.190	15
0.37	8.09	0.046	30
0.40	12.82	0.032	45
0.34	8.21	0.042	60
0.36	8.18	0.044	75

Table D -4: Spiked Sand - 18-08-2005 @ 40oC and 17.2 MPa

Mass of Cu (ug)	CO2 flowed	Cu(ug)/L of CO2	Time
62.87	10.1	6.225	15
57.71	9.53	6.056	30
50.75	8.4	6.042	45
43.90	7.29	6.022	60
17.19	11.6	1.482	75

Table D -5: Spiked Sand - 09-09-2005 @ 40oC and 20.7 MPa

Mass of Cu (ug)	CO2 flowed (L)	Cu(ug)/L of CO2	Time
82.07	12.06	6.805	15
75.00	11.43	6.561	30
78.86	16.39	4.811	45
95.00	10.74	8.845	60
21.87	11.6	1.885	75

Table D -6: Spiked Sand - 28-09-2005 @ 35oC and 24.1 MPa

Mass of Cu (ug)	CO2 flowed (L)	Cu(ug)/L of CO2	Time
68.48	17.19	3.98	15
52.16	18.17	2.87	30
42.63	16.74	2.55	45
29.34	17.57	1.67	60
6.34	6.48	0.98	75

APPENDIX E

APPENDIX E: Results from extraction experiments

Table E-1a: Spiked Silt - 15-08-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1A	71.51	0.02	1.43
Trap 2	2A	40.99	0.0195	0.80
Trap 3	3A	37.46	0.0184	0.69
Trap 4	4A	37.19	0.0165	0.61
Bypass	5A	45.42	0.016	0.73
			Total Cu in the trap =	**4.26**

Table E-1b: Spiked Silt - 15-08-2005 @ 40°C and 17.2 MPa

Soil Samples	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)
Before Ext.	1a	83.05	**41.525**
After Ext. 1	2a	86.23	43.115
2	3a	92.46	46.23
3	4a	79.23	39.615
	Average =	85.97	**42.99**

Table E -2a: Spiked Silt - 16-08-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1B	96.55	0.0175	1.69
Trap 2	2B	52.52	0.0175	0.92
Trap 3	3B	48.14	0.0175	0.84
Trap 4	4B	85.53	0.016	1.37
Bypass	5B	36.57	0.0185	0.68
			Total Cu in the trap =	**5.50**

Table E -2b: Spiked Silt - 16-08-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)
Before Ext.	1b	79.64	**39.82**
After Ext. 1	2b	86.83	43.42
2	3b	81.32	40.66
3	3b	80.09	40.05
	Average =	82.75	**41.37**

Table E -3a: Spiked Silt - 06-09-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1-A	70.955	0.016	1.14
Trap 2	2-A	213.352	0.0155	3.31
Trap 3	3-A	67.7	0.0158	1.07
Trap 4	4-A	87.624	0.0157	1.38
Bypass	5-A	59.33	0.0157	0.93
			Total Cu in the trap =	**7.82**

Table E -3b: Spiked Silt - 06-09-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Average	Mass of Cu (ug)	% Efficiency
Before Ext.	1-a	109.23	104.12	52.06	**3.47**
Before Ext.	2-a	99.01			
After Ext. 1	3-a	105.89	100.51	50.25	
After Ext. 2	4-a	95.124			

Table E -4a: Spiked Silt - 07-09-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1-B	169.34	0.021	3.56
Trap 2	2-B	243.568	0.0157	3.82
Trap 3	3-B	172.275	0.0203	3.50
Trap 4	4-B	247.599	0.0158	3.91
Bypass	5-B	142.52	0.0203	2.89
			Total Cu in the trap =	**17.68**

Table E -4b: Spiked Silt - 07-09-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Average	Mass of Cu (ug)	% Efficiency
Before Ext.	1-b	138.49	116.85	58.43	**7.85**
Before Ext.	2-b	95.217			
After Ext. 1	3-b	119.627	107.68	53.84	
After Ext. 2	4-b	95.723			

Table E -5a: Spiked Sand - 17-08-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1C	1551.036	0.0192	29.78
Trap 2	2C	1661.49	0.0185	30.74
Trap 3	3C	2211.153	0.0165	36.48
Trap 4	4C	2210.337	0.017	37.58
Bypass	5C	0	0	0.00
			Total Cu in the trap =	**134.58**

Table E -5b: Spiked Sand - 17-08-2005 @ 40°C and17.2 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)
Before Ext.	1c	52.11	**26.055**
After Ext. 1	2c	58.936	29.468
2	3c	53.63	26.815
3	4c	63.34	31.67
	Average =	58.64	**29.32**

Table E -6a: Spiked Sand - 18-08-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1D	3698.255	0.017	62.87
Trap 2	2D	3497.866	0.0165	57.71
Trap 3	3D	2950.589	0.0172	50.75
Trap 4	4D	2582.37	0.017	43.90
Bypass	5D	982.501	0.0175	17.19
			Total Cu in the trap =	**232.43**

Table E -6b: Spiked Sand - 18-08-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	% Efficiency
Before Ext.	1d	54.66	27.33	**13.20**
After Ext. 1	2d	49.97	24.99	
2	3d	48.05	24.025	
3	4d	44.31	22.16	
	Average =	47.44	23.72	

Table E -7a: Spiked Sand - 08-09-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1-C	4673.283	0.0158	73.84
Trap 2	2-C	4829.15	0.0153	73.89
Trap 3	3-C	8627.547	0.015	129.41
Trap 4	4-C	2548.986	0.0154	39.25
Bypass	5-C	773.538	0.0157	12.14
			Total Cu in the trap =	**328.54**

Table E -7b: Spiked Sand - 08-09-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Average	Mass of Cu (ug)	% Efficiency
Before Ext.	1-c	58.459	50.828	25.414	**1.49**
Before Ext.	2-c	43.197			
After Ext.	3-c	38.226	50.07	25.04	
After Ext.	4-c	61.917			

Table E -8a: Spiked Sand - 08-09-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1-D	5830.344	0.0156	90.95
Trap 2	2-D	6072.791	0.0157	95.34
Trap 3	3-D	6987.529	0.0153	106.91
Trap 4	4-D	6061.097	0.0154	93.34
Bypass	5-D	909.879	0.0157	14.29
			Total Cu in the trap =	**400.83**

Table E -8b: Spiked Sand - 08-09-2005 @ 40°C and 17.2 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Average	Mass of Cu (ug)	% Efficiency
Before Ext.	1-d	77.169	70.5395	35.27	**36.67**
Before Ext.	2-d	63.91			
After Ext.	3-d	49.116	44.67	22.34	
After Ext.	4-d	40.225			

Table E -9a: Spiked Silt - 13-09-2005 @ 40°C and 20.7 MPa

ample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1-G	975.957	0.015	14.64
Trap 2	2-G	689.631	0.0154	10.62
Trap 3	3-G	710.857	0.0152	10.81
Trap 4	4-G	682.015	0.0153	10.43
Bypass	5-G	205.427	0.0157	3.23
			Total Cu in the trap =	**49.72**

Table E -9b: Spiked Silt - 13-09-2005 @ 40°C and 20.7 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Average	Mass of Cu (ug)	Two-sample t-test
Before Ext.	1-g	112.449	82.68	41.34	$t_o = 0.56$
Before Ext.	2-g	52.904			$\vert t_{critical} \vert = 4.30$
After Ext. 1	3-g	99.161	99.42	49.71	$t_o < t_{crit}$
After Ext. 2	4-g	99.67			No difference

Table E -10a: Spiked Silt - 14-09-2005 @ 40°C and 20.7 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1-H	445.998	0.015	6.69
Trap 2	2-H	395.054	0.0156	6.16
Trap 3	3-H	362.02	0.0157	5.68
Trap 4	4-H	564.139	0.0155	8.74
Bypass	5-H	313.744	0.015	4.71
			Total Cu in the trap =	**31.99**

Table E -10b: Spiked Silt - 14-09-2005 @ 40°C and 20.7 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Average	Mass of Cu (ug)	Two-sample t-test
Before Ext.	1-h	28.894	67.82	33.91	$t_o = 0.56$
Before Ext.	2-h	106.737			$t_{critical}\| = 4.30$
After Ext. 1	3-h	89.245	89.43	44.71	$t_o<t_{crit}$
After Ext. 2	4-h	89.614			No difference

Table E -11a: Spiked Sand - 09-09-2005 @ 40°C and 20.7 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1-E	5260.684	0.0156	82.07
Trap 2	2-E	4838.477	0.0155	75.00
Trap 3	3-E	5222.396	0.0151	78.86
Trap 4	4-E	6050.681	0.0157	95.00
Bypass	5-E	1448.298	0.0151	21.87
			Total Cu in the trap =	**352.79**

Table E -11b: Spiked Sand - 09-09-2005 @ 40°C and 20.7 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Average	Mass of Cu (ug)	% Efficiency
Before Ext.	1-e	79.791	73.9195	36.96	42.75
Before Ext.	2-e	68.048			
After Ext.	3-e	40.315	42.32	21.16	
After Ext.	4-e	44.324			

Table E -12a: Spiked Sand - 12-09-2005 @ 40°C and 20.7 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)
Trap 1	1-F	4591.856	0.0155	71.17
Trap 2	2-F	6891.803	0.0153	105.44
Trap 3	3-F	8140.045	0.0155	126.17
Trap 4	4-F	7129.308	0.0154	109.79
Bypass	5-F	1323.881	0.0155	20.52
			Total Cu in the trap =	**433.10**

Table E -12b: Spiked Sand - 12-09-2005 @ 40°C and 20.7 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Average	Mass of Cu (ug)	% Efficiency
Before Ext.	1-f	74.695	76.3715	38.19	44.89
Before Ext.	2-f	78.048			
After Ext.	3-f	44.489	42.09	21.04	
After Ext.	4-f	39.686			

Table E -13a: Spiked Silt - 05-10-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	DA-1	58.037	0.0185	1.07	0.064
Trap 2	DB-2	18.553	0.02	0.37	
Trap 3	DC-3	18.81	0.0215	0.40	
Trap 4	DD-4	22.391	0.0154	0.34	
Bypass	DE-5	20.062	0.018	0.36	
			Total Cu in the trap =	2.56	

Table E -13b: Spiked Silt - 05-10-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Ad	92.758	46.38	41.93	0.939
2	Bd	80	40.00		
3	Cd	78.832	39.42		
After Ext. 1	Dd	81.087	40.54	41.54	
2	Ed	86.63	43.32		
3	Fd	81.507	40.75		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
1.07	0.000001	5.67	8.97E-09

Table E -14a: Spiked Silt - 19-10-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	EA-1	42.8	0.019	0.81	0.117
Trap 2	EB-2	68	0.0154	1.05	
Trap 3	EC-3	49.8	0.0187	0.93	
Trap 4	ED-4	78.95	0.018	1.42	
Bypass	EE-5	25.56	0.0185	0.47	
			Total Cu in the trap =	4.69	

Table E -14b: Spiked Silt - 19-10-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Ae	91.4	45.70	45.40	2.122
2	Be	88.78	44.39		
3	Ce	92.2	46.10		
After Ext. 1	De	86.5	43.25	44.43	
2	Ee	92.20	46.10		
3	Fe	87.9	43.95		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
0.81	0.0000008	8.38	4.59E-09

Table E -15a: Spiked Silt - 20-10-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	FA-1	9.28	0.016	0.15	0.016
Trap 2	FB-2	9.93	0.016	0.16	
Trap 3	FC-3	5.62	0.0165	0.09	
Trap 4	FD-4	6.1	0.019	0.12	
Bypass	FE-5	9.18	0.0155	0.14	
			Total Cu in the trap =	**0.66**	

Table E -15b: Spiked Silt - 20-10-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Af	93.47	46.74	45.78	0.899
2	Bf	91.2	45.60		
3	Cf	90	45.00		
After Ext. 1	Df	90	45.00	45.37	
2	Ef	92.80	46.40		
3	Ff	89.4	44.70		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
0.15	0.0000002	4.9	1.46E-09

Table E -16a: Spiked Sand - 28-09-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	AA-1	3476.256	0.0197	68.48	
Trap 2	AB-2	2789.45	0.0187	52.16	
Trap 3	AC-3	2715.449	0.0157	42.63	
Trap 4	AD-4	1868.535	0.0157	29.34	
Bypass	AE-5	389.13	0.0163	6.34	
			Total Cu in the trap =	**198.96**	**4.974**

Table E -16b: Spiked Sand - 28-09-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Aa	107.245	53.62		
2	Ba	54.2	27.10		**56.815**
3	Ca	233.344	116.67	65.80	
After Ext. 1	Da	69.98	34.99		
2	Ea	51.26	25.63		
3	Fa	49.25	24.63	28.42	

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
68.48	0.000068	17.19	1.89E-07

Table E -17a: Spiked Sand - 29-09-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	BA-1	7710.632	0.0149	114.89	
Trap 2	BB-2	5448.858	0.02	108.98	
Trap 3	BC-3	3296.263	0.0187	61.64	
Trap 4	BD-4	5641.374	0.0187	105.49	
Bypass	BE-5	1380.496	0.014	19.33	
			Total Cu in the trap =	**410.33**	**10.258**

Table E -17b: Spiked Sand - 29-09-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Ab	53.899	26.95	28.99	0.769
2	Bb	61.618	30.81		
3	Cb	58.4	29.20		
After Ext. 1	Db	60.49	30.25	28.76	
2	Eb	60.59	30.30		
3	Fb	51.5	25.75		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
114.89	0.000115	18.68	2.92E-07

Table E -18a: Spiked Sand - 03-10-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	CA-1	11483.15	0.0146	167.65	12.760
Trap 2	CB-2	7223.973	0.017	122.81	
Trap 3	CC-3	6331.06	0.0167	105.73	
Trap 4	CD-4	6533.312	0.0152	99.31	
Bypass	CE-5	1027.887	0.0145	14.90	
			Total Cu in the trap =	**510.40**	

Table E -18b: Spiked Sand - 03-10-2005 @ 35°C and 24.1 MPa

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Ac	92.5	46.25	45.46	36.389
2	Bc	36	18.00		
3	Cc	144.232	72.12		
After Ext. 1	Dc	84.288	42.14	28.91	
2	Ec	43.20	21.60		
3	Fc	46	23.00		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
167.65	0.000168	17.39	4.58E-07

Table E -19a: **Spiked Silt - 16-11-2005 @ 35°C and 24.1 MPa (tta+TBP)**

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	JA-1	410.127	0.019	7.79	
Trap 2	JB-2	53.495	0.0184	0.98	
Trap 3	JC-3	47.4	0.0172	0.82	
Trap 4	JD-4	47.55	0.014	0.67	
Bypass	JE-5	38.87	0.0156	0.61	
			Total Cu in the trap =	**10.86**	**0.272**

Table E -19b: **Spiked Silt - 16-11-2005 @ 35°C and 24.1 MPa (tta+TBP)**

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	Two-sample t-test
Before Ext.1	Aj	171.866	85.93	60.60	$t_o = 0.43$
2	Bj	98.152	49.08		$t_{crit} = 2.78$
3	Cj	93.598	46.80		to<tcrit
After Ext. 1	Dj	169.57	84.79	67.21	P-value = 0.7
2	Ej	118.84	59.42		No difference
3	Fj	114.861	57.43		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
7.79	0.0000078	13.05	2.84E-08

Table E -20a: **Spiked Silt - 18-11-2005 @ 35°C and 24.1 MPa (tta+TBP)**

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	KA-1	58.71	0.0156	0.92	
Trap 2	KB-2	45.17	0.0155	0.70	
Trap 3	KC-3	34.6	0.017	0.59	
Trap 4	KD-4	30.035	0.0163	0.49	
Bypass	KE-5	15.18	0.0177	0.27	
			Total Cu in the trap =	**2.96**	**0.074**

Table E -20b: Spiked Silt - 18-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	Two sample t-test
Before Ext.1	Ak	126.965	63.48	52.41	$t_o = 0.31$
2	Bk	90.498	45.25		$t_{crit} = 2.78$
3	Ck	97	48.50		to<tcrit
After Ext. 1	Dk	154.33	77.17	56.08	P-value = 0.774
2	Ek	89.76	44.88		No difference
3	Fk	92.36	46.18		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
0.92	0.0000009	10.69	4.09E-09

Table E -21a: Spiked Silt - 18-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	LA-1	41.09	0.019	0.78	
Trap 2	LB-2	55.58	0.0187	1.04	
Trap 3	LC-3	101.38	0.0193	1.96	
Trap 4	LD-4	54.4	0.0179	0.97	
Bypass	LE-5	172.43	0.0147	2.53	
			Total Cu in the trap =	**7.29**	**0.182**

Table E -21b: Spiked Silt - 18-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	Two sample t-test
Before Ext.1	Al	94.81	47.41	47.06	$t_o = 1.80$
2	Bl	93.23	46.62		$t_{crit} = 2.78$
3	Cl	94.34	47.17		to<tcrit
After Ext. 1	Dl	107.67	53.84	52.94	P-value = 0.15
2	El	93.80	46.90		No difference
3	Fl	116.18	58.09		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
0.78	0.0000008	10.69	3.47E-09

Table E -22a: Spiked Sand - 22-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	GA-1	6543.034	0.0167	109.27	10.727
Trap 2	GB-2	6060.599	0.0184	111.52	
Trap 3	GC-3	5478.604	0.0183	100.26	
Trap 4	GD-4	5723.88	0.0167	95.59	
Bypass	GE-5	740.178	0.0168	12.43	
			Total Cu in the trap =	**429.07**	

Table E -22b: Spiked Sand - 22-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Ag	77.376	38.69	35.60	**31.508**
2	Bg	70.05	35.03		
3	Cg	66.188	33.09		
After Ext. 1	Dg	49.111	24.56	24.38	
2	Eg	46.10	23.05		
3	Fg	51.1	25.55		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
109.27	0.000109	23.03	2.26E-07

Table E -23a: Spiked Sand - 14-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	HA-1	8065.804	0.0157	126.63	14.227
Trap 2	HB-2	11337.869	0.014	158.73	
Trap 3	HC-3	8758.082	0.0163	142.76	
Trap 4	HD-4	7756.184	0.0157	121.77	
Bypass	HE-5	1177.61	0.0163	19.20	
			Total Cu in the trap =	**569.09**	

Table E -23b: Spiked Sand - 14-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Ah	105.662	52.83	42.27	27.886
2	Bh	79.54	39.77		
3	Ch	68.42	34.21		
After Ext. 1	Dh	64.66	32.33	30.48	
2	Eh	42.40	21.20		
3	Fh	75.84	37.92		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
126.63	0.000127	18.94	3.18E-07

Table E -24a: Spiked Sand - 15-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	IA-1	10599.551	0.0163	172.77	14.524
Trap 2	IB-2	7919.378	0.0157	124.33	
Trap 3	IC-3	6915.941	0.0167	115.50	
Trap 4	ID-4	8931.847	0.0169	150.95	
Bypass	IE-5	1160.009	0.015	17.40	
			Total Cu in the trap =	**580.95**	

Table E -24b: Spiked Sand - 15-11-2005 @ 35°C and 24.1 MPa (tta+TBP)

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Ai	80.4	40.20	39.55	21.513
2	Bi	77.78	38.89		
3					
After Ext. 1				31.04	
2	Ei	63.85	31.93		
3	Fi	60.3	30.15		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
172.77	0.000173	23.44	3.50E-07

Table E -25a: Spiked Silt - 24-11-2005 @ 35°C and 24.1 MPa (tta+TBP+10%H2O)

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	NA-1	4878.233	0.017	82.93	**5.308**
Trap 2	NB-2	2840.78	0.019	53.97	
Trap 3	NC-3	1378.3	0.0174	23.98	
Trap 4	ND-4	2344.765	0.0175	41.03	
Bypass	NE-5	593.94	0.0175	10.39	
			Total Cu in the trap =	**212.31**	

Table E -25b: Spiked Silt - 24-11-2005 @ 35°C and 24.1 MPa (tta+TBP+10%H2O)

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	An	99.317	49.66	48.55	12.463
2	Bn	94.5	47.25		
3	Cn	97.49	48.75		
After Ext. 1	Dn	88.26	44.13	42.50	
2	En	81.30	40.65		
3	Fn	85.44	42.72		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
82.93	0.0000829	25.02	1.58E-07

Table E -26a: Spiked Sand - 22-11-2005 @ 35°C and 24.1 MPa (tta+TBP+10%H2O)

Sample	Sample ID	Conc. Of Cu in 10ml digested sample (ug/L)	Total Volume (L)	Mass of Cu (ug)	% Ext.efficiency
Trap 1	MA-1	12448.986	0.0168	209.14	**16.182**
Trap 2	MB-2	9763.446	0.0166	162.07	
Trap 3	MC-3	8621.481	0.0167	143.98	
Trap 4	MD-4	6042.754	0.0175	105.75	
Bypass	ME-5	1791.779	0.0147	26.34	
			Total Cu in the trap =	**647.28**	

Table E -26b: Spiked Sand - 22-11-2005 @ 35°C and 24.1 MPa (tta+TBP+10%H2O)

Sample	Sample ID	Conc. Of Cu (ug/L)	Mass of Cu (ug)	Average	% Efficiency
Before Ext.1	Am	85.864	42.93	35.99	11.877
2	Bm	48.54	24.27		
3	Cm	81.51	40.76		
After Ext. 1	Dm	94.58	47.29	31.71	
2	Em	53.92	26.96		
3	Fm	41.77	20.89		

Mass of Cu (ug)	Mass of Cu (g)	Volume of CO_2 (L)	Solubility
209.00	0.000209	19.55	5.08E-07

APPENDIX F

APPENDIX F: Sample calculations for the solubility

The solubility of $Cu(tta)_2$ can be calculated from the amount of $Cu(tta)_2$ present in the solvent traps and CO_2 flowed through the traps. The solubility is calculated as follows:

$$S = \frac{m_{Cu(tta)_2}..M_{CO_2}}{V_{CO_2}.D_{CO_2}.M_{Cu(tta)_2}}$$

In the above equation S represent solubility, m is the mass of $Cu(tta)_2$ in the solvent trap and M_{Co2} is the molar mass of CO_2. V denotes the volume of CO_2 flowed through the traps, D is the density of Sc-CO_2 and $M_{Cu(tta)2}$ is the molar mass of $Cu(tta)_2$.

The density of CO_2 at room temperature and pressure can be calculated as follows:

$$D = \frac{MP}{RT}$$

Where,

M = Molar mass of CO_2 (44.01g/mole)

P = Pressure (102.325 * 10^3 Pa)

R = Gas constant (8.414J/mole-K)

T = Temperature (273.15K)

So at 20°C the desity of CO_2 is:

$$D = \frac{(44.01g/mole)(101.325\times10^3 Pa)}{(8.414J/mole-K)(293.15K)}$$

D = 1.829Kg/m3

Or D = 1.829g/L

The solubility for the Spiked sand extraction 2005-10-03 @ 24.1 MPa and35°C is given below:

$m_{Cu(tta)2} = 1.68*10^{-3}$g and V_{CO2} = 17.39L

$$S = \frac{(1.68\times10^{-3} gCu(tta)_2)(44.01gCO_2/molCO_2)}{(17.39LCO_2)(1.83gCO_2/LCO2)(505.9gCu(tta)_2/molCu(tta)_2}$$

S = 4.58 x 10^{-7} g $Cu(tta)_2$/ g CO_2

APPENDIX G

APPENDIX G: Raw Data for Cumulative mass of Cu collected during SC CO_2 extraction

Table G-1: Cumulative mass of Cu collected with Cumulative mass of SC CO_2

Rum Time (min)	Total Flow (ml/min)	Volume of CO_2 (ml)	Mass of CO_2(g)	Cumulative mass of CO_2(g)	Mass of Cu (ug)	Mass of Cu (g)	Cumulative mass of CO_2(g)
0							
60							
75	2	30	30	30	17.71	0.000018	0.000018
90	3	45	45	75	105.44	0.000105	0.000123
105	3.5	52.5	52.5	127.5	126.17	0.000126	0.000249
120	2.9	43.5	43.5	171	109.79	0.000110	0.000359
135	2.2	33	33	204	20.52	0.000021	0.000380