INVESTIGATION OF THE EFFECTS OF POLYCHLORINATED BIPHENYL (PCB) DECHLORINATION ON THE NATURAL INHIBITORS AND OXIDATION STABILITY OF UNINHIBITED NAPHTHENIC BASED MINERAL OILS

Sumaya Nassiep

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Supervisor: Prof Dave Arnold

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ABSTRACT

PCBs are persistent organic pollutants that have intentionally and unintentionally (through contamination) been added to mineral insulating oil to improve its insulating and cooling properties within electrical equipment. The Stockholm Convention on Persistent Organic Pollutants (2001) orders the eradication of PCBs from use by 2025.

Sodium based dechlorination is a PCB destruction process that is non-thermal, relatively cost effective and allows for the recovery of a reusable end product. A comparative benefits study, contained in chapter 2 of this dissertation, describes the increased financial and environmental impact associated with incinerating large volumes of PCB contaminated mineral oil. The results of the comparative analysis indicate a cost ratio of 1: 2.5, in favour of sodium dechlorination.

In addition to the financial benefit, the sodium based PCB dechlorination process is versatile and can be either batched or skid mounted and is typically combined with an oil regeneration step, allowing for transformers to be treated onsite and whilst energised. Eskom is currently considering obtaining the mobile dechlorination unit for the purpose of conducting dechlorination and regeneration on its PCB contaminated transformers while energised.

Mineral insulating oil is considered a strategic asset within most industries. Eskom uses mainly uninhibited mineral oil in its older transformers and the effects of PCB dechlorination on the natural inhibitor content of the oil is uncertain.

The objective of this study was to investigate the effects of sodium dechlorination on the oxidation stability and thereby indirectly the natural inhibitor content of uninhibited naphthenic based mineral oil. The study involved the dechlorination, regeneration and subsequent chemical analyses of PCB contaminated oils in the PCB ranges <50ppm, 50 to 500 ppm and >500 ppm as stipulated by the Stockholm Convention on Persistent Organic Pollutants (2001).

The study confirmed the reduction in oxidation stability and thereby the natural inhibitor content of the mineral oil after sodium dechlorination. Based on the results obtain a

preliminary algorithm was established to predict the reduction in oxidation stability after sodium dechlorination, as a function of the PCB concentration prior to dechlorination. This will provide an indirect indication of the rate of natural inhibitor depletion of the oil, based on its exposure to the sodium dechlorination reagents and process conditions.

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DEFINITIONS

Abnormal Operating Conditions	Transformer operations where the mineral insulating oils is exposed to high temperatures and excess moisture and oxygen
Age assessment tests	Age assessment tests are done to determine the ageing characteristics of electrical equipment by means of chemical analysis of the insulating oil.
Antioxidant additive	A synthetic organic compound added to retard the oxidation process in insulating oil.
Arrhenius law	A mathematical empiric law relating to the influence of temperature on the velocity of chemical reactions.
Askarel and Aroclor	Refers to well defined commercial PCB mixtures.
Backpropagation	A supervised learning process for training feed forward neural networks to learn from test samples
Concentration:	Refers to the concentration of PCBs in the dilutent in mg/L or parts per million.
Congeners	Group of chemicals which have the same basic structure.
Corrosive sulphur:	Oil containing reactive sulphur that can cause corrosion problems in power equipment.
Dechlorinated oil	PCB contaminated oil which has passed through a chlorine stripping chemical process and has been treated in such a manner so as to render it safe and no longer a safety, health and environmental hazard.
Duty of Care (National Environmental Management Act)	An ethical and legal concept relating to the responsibility of each and every individual to take all reasonable and practical measures in undertaking their activities to prevent harm to another person or property of another
Dielectric strength	Ability of oil to withstand electrical stress, and is influenced by the presence of moisture and particulate material in the oil
Electrical equipment:	Transformer, capacitor, voltage regulator, re-closer, switchgear or cable that contains dielectric fluid

Gigawatt hour	1000 x MWh
Inhibited	Insulating oil that has a synthetic antioxidant additive added to prevent oxidation. Typical values are between a minimum of 0.08% to a maximum of 0.4% anti oxidant.
Insulating (mineral) oil	Mineral oil used in transformers and other electrical equipment for insulation and cooling.
Kilowatt hour	The unit of energy equivalent to one kilowatt (1 kW) of power expended for one hour (1 h) of time
Megaflex	Time of use electricity tariff for urban customers who are able to shift load and with an NMD (notified maximum demand) greater than 1MVA
Megawatt hour	1000 x kWh
Moisture content	Moisture dissolved in oil and measured in parts per million or milligrams per kilogram. Moisture decreases the insulating potential of oil and can originate from sources both internal and external to electrical equipment.
Miniflex	Time of use electricity tariff for urban customers with an NMD from 25kVA up to 5MVA (font)
Naphthenic, paraffinic or aromatic insulating oil	Classification of oil dependent on the relative proportions of the three molecular types, each of which conveys its own properties of the finished product.
Neutralization value, acidity, total acid number	Indication or measure of the acidic constituents or contaminants in the oil. The presence of acids is normally an indication of oxidation of oil.
New /Virgin oil	Oil that has never been used in electrical equipment and that complies in all respects with new oil specifications laid down in this document.
Non-PCB	Oil, including oil in electrical equipment and in any item of equipment, that has a measurable PCB concentration of less than <50 ppm as per SANS 0290
Oxidation	Process of oil degradation induced by the presence of moisture, oxygen and high temperatures.
Polychlorinated Biphenyl	Any one of a number of 209 congeners containing one to ten chlorine atoms attached to a biphenyl group.

	PCBs are synthetic products not known to occur naturally. New oil produced from crude oil does not contain PCB.
PCB contaminated item	Equipment or container (e.g. package, can, bottle, bag, barrel, drum, tank) or any other device that contains PCB or the surfaces of which have been in contact with PCB (the PCB being at a concentration of between 51 ppm and 500 ppm), or any article (e.g. container, oil, water, soil, personal protective equipment) that has been in contact with PCB or PCB contaminated equipment
PCB free	PCB level is below the detection limits and ideally will be zero
Regeneration process	A clay reclamation process whereby the chemical and physical properties of used oil is restored to SANS 10555 standards
Regenerated oil	Reclaimed used oil that has undergone an oil regeneration process.
Single layer perceptron	A simple net that can decide if an input belongs to one of two possible classes.
Transformer	A static electrical device that transfers electricity from one electrical circuit to another by magnetic coupling. It is often used to convert between high and low voltages and accordingly between low and high currents.
Uninhibited	Insulating oil that has no antioxidant additive present and therefore depends on its natural antioxidants to combat oxidation.

ABBREVIATIONS

COP	Conference of parties
DBDS	Dibenzyl disulphide
DEA	Department of environmental affairs (South Africa)
DGA	Dissolved gas analysis
GWh	Giga Watt hour
H:H	Landfill site licensed to dispose of highly hazardous materials
HPLC	High performance liquid chromatography
kWh	Kilowatt hour
MWh	Mega Watt hour
mg KOH/g	Amount of potassium hydroxide, measured in milligrams, needed to neutralize the amount of acid in a weighed amount of oil.
PAH	Polyaromatic hydrocarbon(s)
PCB	Polychlorinated biphenyl
POP	Persistent organic pollutant
ppm	Parts per million
SANS	South African national standards
TNP	Test not performed
UNEP	United nations environmental programme

Chapter One

INTRODUCTION

1.1 BACKGROUND

Polychlorinated Biphenyl (PCB) is the generic term given to a broad class of fire-resistant synthetically produced substances. PCBs were designed to have very high physical and chemical stability which created ideal heat transfer and electrical insulating media for a host of industrial and commercial applications, the most common being its use in electrical equipment such as transformers and capacitors.

Sanders *et al.* (1992) cited that the first commercial production of PCBs dated back to the late 1920's, which sparked its global demand and production under various trade names during the five decades that followed. The most common PCB trade name encountered in South Africa is Askarel, which consists of a combination of commercial PCB mixtures. Globally, PCB production ceased in the late 1970's after it was confirmed that the very characteristics that made them ideal for industrial use also rendered them problematic to human health and the environment (US EPA, n.d).

PCBs have been earmarked under the Stockholm Convention on Persistent Organic Pollutants for eradication from the environment by 2025. The convention was ratified by the South African government on the 4th of September 2002, as stated by the United Nations Environmental Programme (UNEP) in its Status of ratification of the Stockholm Convention report (UNEP, 2006). South Africa is a party to the convention and has consented to be bound by the regulations and terms of the convention. All industries within South Africa are legally required to conform to the conditions, restrictions and limitations as set out in the convention. The South African DEA, in collaboration with the Stockholm Convention's implementing body, UNEP, has initiated a PCB inventory collection campaign. The immediate objective of the campaign is to establish registers of PCB stockpiles from major industries and to create awareness within industry. The long term objective of the inventory collection campaign is to regulate and monitor the management and safe disposal of PCBs within the timeframe stipulated by the Stockholm Convention. This is done in accordance with the terms as set in Article 6 of the convention (Stockholm Convention, 2001).

Several PCB disposal processes based on thermal, chemical and microbial destruction techniques are in commercial use worldwide. Only two disposal options are currently legally available within South Africa namely, land filling at a licensed H:H landfill site and thermal treatment at a licensed hazardous disposal plant in Gauteng. Section 20 of the Environment Conservation Act (1989) of South Africa declares that waste can only be disposed of at facilities that are licensed by the Minister of the then Water Affairs and Forestry Department. Fulfillment of the requirements for the licensing of a hazardous waste treatment facility are, understandably, exponentially more stringent, extensive and therefore costly when compared to that of a general waste processing facility or site. This is a major contributing factor to the limited number of licensed PCB disposal options available within South Africa.

1.2 THE PCB SITUATION IN ESKOM

Eskom purchased several thousand PCB capacitors and very few PCB containing transformers, mainly excitation type, during the 1900's. The power utility's access to the widespread acquisition of PCB containing equipment was relatively limited as a result of sanctions imposed upon South Africa during the Apartheid years. Eskom has taken a proactive approach to the identification, management and environmentally sound disposal of its PCB stockpiles over the past two decades. This is evident in its 1993 establishment of a PCB test laboratory, its 1995 hosting of an International Conference on PCBs, the development of in-house PCB expertise and the implementation of several PCB directives, policies, specifications and standards within the utility. Despite these efforts, Eskom still has in excess of 1000 tons of PCB containing equipment and a few thousand tons of PCB contaminated oil requiring phase-out. The utility's phase-out plans have been hampered by a number of factors. These include;

- The limited number of licensed PCB disposal facilities available locally. Disposal options are currently restricted to land filling or thermal treatment.

- No availability of a government licensed PCB dechlorination facility. Dechlorination would allow for the recovery and reuse of the dechlorinated oil, be it for reuse internally and/or externally to the Eskom network.

- The high costs associated with currently available disposal options. The licensed PCB disposal facilities currently have a monopoly within their respective markets.

- Eskom's current financial and electricity supply constraints, warranting the prioritisation of critical areas to ensure business sustainability viz. capital expansion planning, new build, and optimisation of operations and maintenance regimes.

1.3. POTENTIAL ALTERNATIVE USES OF DECHLORINATED OILS

As a result of the uncertainty regarding the reuse of uninhibited dechlorinated mineral oil within the Eskom transformer fleet, establishing potential alternative uses for such oils is of importance to Eskom. The author consulted with in-house specialists on the Eskom Insulating Oil Steering Committee to establish possible alternative uses, i.e. other than its use in transformers. The option of adding an artificial inhibitor after dechlorination and then its reuse in transformers was considered. Eskom uses predominantly laboratory analyses for condition monitoring of its transformers. Artificially inhibiting the oil may affect its in-service behaviour, which in turn will have an effect on transformer trending patterns.

Potential alternative uses for dechlorinated oils include:

- Blending as a co-fuel in other processes such as cement kilns, dual fuel boilers (depending on oil characteristics), etc.
- As top-up oil for transformers containing uninhibited oils and provided it conforms to the SANS 555 standard (SABS, 2007).
- Use in lubricating oils
- Use in smaller non-critical electrical equipment such as pole mounted transformers
- In the production of petroleum based products.

In light of the recent global crude oil crisis and shortage, the reuse of the recovered oils will offer some financial relief to industry.

1.4. EXPECTED BENEFITS

The expected benefits of this study to Eskom and Industry are summarised as follows:

- The study provides the scientific basis to confirm the research hypothesis and therefore to discourage the use, and or reuse, of sodium based dechlorinated uninhibited naphthenic mineral oils in critical electrical equipment such as transformers. Doing so may result in accelerated ageing through increased rates of oil and cellulose oxidation and ultimately reduce the operational life expectancy of the transformers.

- Improved economic benefit through promotion of the reuse of dechlorinated oil in other areas internal or external to the business and in so doing offset the cost of PCB dechlorination.

- Positive environmental impact as the dechlorination process is a non-thermal PCB destruction method and the oil will be recovered for reuse.

- Will support Eskom's and government's objectives of PCB phase-out in terms of its 2025 Stockholm Convention commitment.

1.5. HYPOTHESIS

Dechlorination of PCB contaminated oils will deplete the uninhibited mineral oils of their natural inhibitors, thereby resulting in reduced oxidation stability and ultimately reduced life expectancies of transformers in which such oils are used and or reused.

1.6. RESEARCH DESIGN

In order to achieve the objective of the study, the author undertook a quantitative research approach. The study used data obtained from various analytical procedures as a basis for verification of the study hypothesis.

The study involves the use of used uninhibited naphthenic based mineral insulating oils as this is typically the type of oil within the Eskom network that would require dechlorination. The characteristics of the oils have been assessed before and after dechlorination through various chemical analyses. The samples stipulated in the study proposal have been subjected to a range of laboratory analytical methods to assess the effects of the sodium based dechlorination on the chemical properties of uninhibited naphthenic based mineral oil. The test results were used to derive a preliminary algorithm to predict the reduction in oxidation stability, after sodium dechlorination, as a function of PCB concentration prior to dechlorination. This will provide an indirect indication of rate of natural inhibitor depletion of the oil based on its exposure to the sodium dechlorination reagents and process conditions.

1.7. RESEARCH METHODOLOGY

The following activities were undertaken by the author during execution of this study:

- Identified a research topic based on current unknowns within the transformer operations and maintenance area of the Eskom business.

- Undertook preliminary investigation into the study topic and produced a full proposal for the study which was reviewed and accepted by the Higher Degree's Committee of the University of Kwa-Zulu Natal.

- Gathered and reviewed literature on uninhibited mineral insulating oil, oxidation stability, polychlorinated biphenyls and Polychlorinated Biphenyl dechlorination processes.

- Identified industry partners, both locally and abroad, with dechlorination technologies to assist in the experimental test trials of this study.

- Collected and prepared sufficient volumes PCB contaminated oils in the relevant PCB concentration levels for use during PCB dechlorination.

- Processed the samples on the sodium dechlorination and collected representative samples for analytical testing of selected oil parameters to assess the oxidation stability of the oil. Samples were taken before and after dechlorination and after oil regeneration.

- The samples were submitted to accredited analytical laboratories, within and external to Eskom, for the following analyses.

    - PCB Analysis
    - Oxidation Stability
    - PAH Analysis
    - Percentage Total Sulphur
    - Karl-Fischer Moisture Content
    - Acidity Content
    - Dielectric Strength

- Evaluation and interpretation of the test results and the derivation of a preliminary algorithm to predict the reduction in oxidation stability after sodium dechlorination, as a function of PCB concentration prior to dechlorination. This will provide an indirect indication of natural inhibitor depletion of the oil based on its exposure to the sodium dechlorination process conditions.

- Conclusions and recommendations based on the findings of the study.

1.8. OUTLINE OF DISSERTATION CHAPTERS

The purpose of this dissertation is to:

- Provide a scientific basis, through literature and experimental studies, to support or reject the study hypothesis that sodium based dechlorination removes the natural inhibitor contained in uninhibited naphthenic based mineral oils.

- To establish a preliminary set of algorithms to provide an indirect measure of the natural inhibitor content of uninhibited naphthenic based mineral oil after PCB dechlorination.

Chapter 1: Provides an introduction by means of a study background, an overview of the PCB situation within Eskom and a comparative cost analysis of licensed PCB processes within South Africa.

Chapter 2: Provides a review of literature relevant to the research topic.

Chapter 3: Describes the experimental methodology employed, provides details on the technical operation of the sodium dechlorination plant and describes the analytical methods used for analyses of PCB dechlorinated oils.

Chapter 4: Presents the experimental results obtained and the evaluation and interpretation thereof.

Chapter 5: Describes the preliminary set of algorithms to predict the natural inhibitor content or the oil after dechlorination.

Chapter 6: Concludes this research relating to the topic.

REFERENCES

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Chapter Two

LITERATURE REVIEW

2.1. INTRODUCTION TO THE LITERATURE REVIEW

Mineral oil serves both a cooling and insulating purpose within transformers. It is for this reason that maintaining the quality of this strategic asset is vitally important to the smooth operation of Eskom’s transformers and ultimately its continuity of supply.

PCBs are persistent organic pollutants that have entered the Eskom oil pool primarily through cross contamination arising from oil rehabilitation processes such as filtration and regeneration. Eskom has an estimated 2 million litres of PCB oil that requires phase-out by 2025. PCB oil dechlorination is a more economical and environmentally sound manner of destroying PCBs while allowing for the recovery of reusable dechlorinated oil. The impact of the process on the natural inhibitors of uninhibited naphthenic based mineral oil was not well publicised. This chapter will review literature relevant to the research topic and will include literature on mineral insulating oils, oxidation of mineral oils, PCBs, Base Catalysed Dechlorination and alternative destruction methods for PCBs in mineral oil.

2.2. MINERAL INSULATING OILS

2.2.1 BASIC CHEMICAL STRUCTURES OF MINERAL INSULATING OIL

Mineral oils are produced from natural crude oil distillates and have complex compositions comprising more than 3000 different hydrocarbons structures as cited by Lobeiras *et al.* (2001). These hydrocarbon structures can be classified under three main hydrocarbon groups namely, straight chains (paraffin’s), rings without double bonds (naphthenes) and/or rings with double bonds (aromatics).

Nynas (2001) describes how the three basic hydrocarbon groups are further divided into straight-chain and branched (iso) paraffin's, mono and condensed naphthenes and mono, linear and angular condensed aromatics. Condensed compounds comprise two or more ring structures in which adjacent rings share two or more carbon atoms. The condensed compounds are important because those which are unsaturated (containing double bonds) are, in general more reactive and therefore affect the physical properties of the oil.

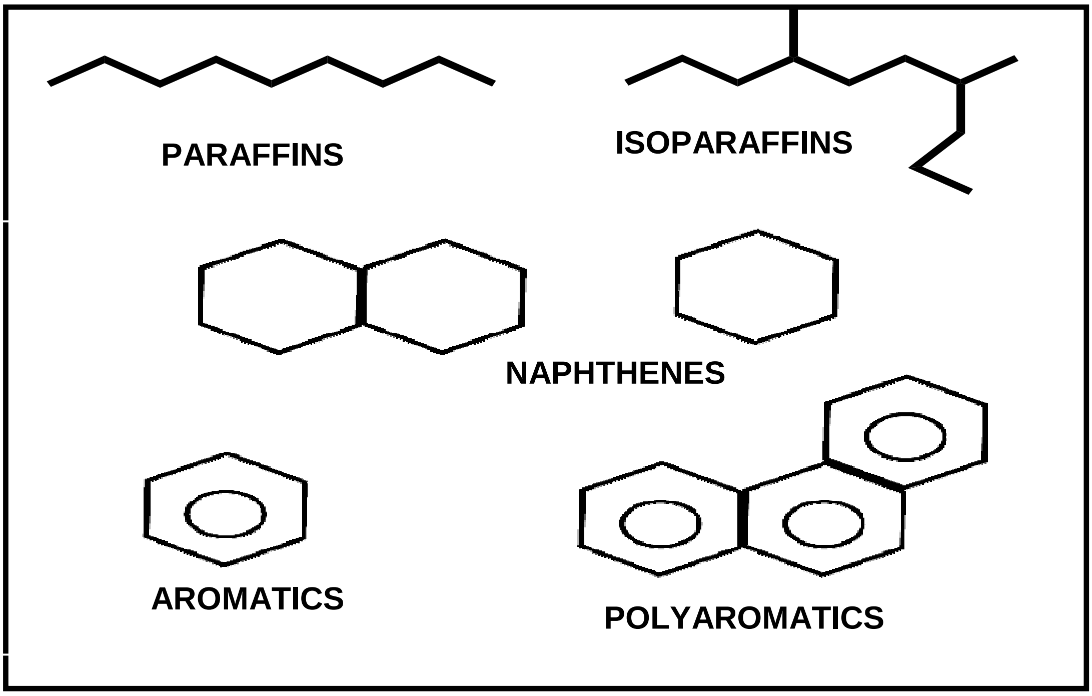


Figure 2-1: Basic hydrocarbon structures in mineral insulating oil (Nynas, 2001)

A mineral oil can be classified as paraffinic, naphthenic or aromatic depending on the relative proportions of the molecular types present in the oil. Each molecular type contributes its own properties to the finished product.

2.2.2 OXIDATION INHIBITORS IN MINERAL OIL

Lewand (2002) explained that mineral insulating oil has molecules that contain atoms other than carbon and hydrogen. These include atoms of sulphur, nitrogen and oxygen which are referred to as heteroatoms. Molecules that have heteroatoms attached to several aromatic rings are known to be highly reactive, oxidise fast and increase the rate of oxidation of other substances. These types of molecules are considered the natural inhibitors within the oil. Inhibitors, whether natural or synthetic, are substances that retard or render the process of oxidation inactive.

Lewand (2002) further mentions that five types of sulphur compounds are generally present in refined transformer oil ranging from corrosive or reactive to very stable depending on the position of the sulphur within the oil's chemical structure. The more the sulphur is bonded, surrounded or contained within a molecule, the less reactive that sulphur becomes.

Table 2-1: Sulphur types and reactivity within mineral oil (Lewand, 2002)

Sulphur Groups	Reactivity
Elemental (free) sulphur	Corrosive
Mercaptans (thiols)	Corrosive
Sulphides (thio-ethers)	Reactive
Disulphides	Stable
Thiophenes	Very Stable

Certain sulphur compounds, in particular stable types, act as natural inhibitors and therefore aid the oxidation stability of the transformer oil. At high temperatures more stable compounds such as disulphides and thiophenes tend to break down to less complex structures causing the formation of reactive or free sulphur. A separate study on the destruction of the artificial sulphur based inhibitor Dibenzyl Disulphide (DBDS), undertaken by Lewand (2008), cites DBDS as a precursor to corrosive sulphur compounds such as DBDS mercaptans. Lewand (2008) further claims that the sodium based dechlorination, using sodium hydroxide as reagent, successfully removed DBDS. The author hypothesises that the process is not selective to only artificial sulphur based inhibitors and that in uninhibited mineral oils (depending on the amount of reagent and sufficient reaction time) the sodium based dechlorination process will result in the reaction of more stable oxidation inhibiting sulphur compounds to form potential corrosive sulphur compounds.

Dalton (2008) and Nynas (2001) explain that mineral oils contain a certain amount of natural inhibitors, consisting of compounds of sulphur, phenols and a smaller amount of nitrogen bounded compounds, however additional artificial inhibitors may be added to oil. The most commonly used artificial inhibitor is Di-isobutyl-para-cresol (DBPC), also known as Butylated hydroxytoluene (BHT).

Historically, Eskom uses mainly uninhibited naphthenic based oils as insulating and cooling media in its older transformer fleet. As the name suggests, these oils contain mainly naphthenic structures with no artificial oxidation inhibitors and depend purely on the oil's natural inhibitors as protection against oil oxidation/ degradation. The use of uninhibited oils is likely to continue in future as Eskom transformers are subjected to periodic oil analyses as a means of condition based monitoring. The data from the oil analyses is used to trend transformer ageing and fault detection. The use of inhibited transformer oils will render the years of laboratory data null and void as inhibited oils age differently to uninhibited oils. Eskom has however purchased inhibited oils for its new fleet of transformers.

2.3. THE ROLE OF MINERAL OIL IN TRANSFORMERS

Mineral oil has two main functions within transformers namely, cooling and insulating. Cooling typically occurs through heat dissipation resulting from power losses and localised hotspots within the transformer, while insulating electrically, as it is a liquid dielectric and fully saturates the solid insulation of the transformer as explained by Meshkatoddini (2008).

The analogy drawn by experts in this field is that mineral oil in a transformer is much like the blood in a human body, where specific characteristics and changes within the oil can be linked to specific developing and existing faults within the transformer. It is for this reason that transformer oil sampling and analyses forms a critical part of any transformer maintenance regime. This allows transformer engineers and operators to trend transformer ageing and allows for the early identification of incipient faults. Furthermore, it also allows for the trending of transformer oil quality and specific analyses are used as indicators for transformer oil changes or regeneration as failure to maintain oil quality can lead to transformer failure (Dalton 2008: Nynas 2001).

In order to achieve optimal performance, the uninhibited mineral oil is required to conform to a specific set of characteristics. Table 2-2 lists the typical chemical analyses performed on regenerated uninhibited mineral oil, the corresponding oil characteristic it measures and the limit for each of the characteristics measured (Dalton 2008: Nynas 2001). The limits for new uninhibited mineral oils are similar to those for regenerated uninhibited oils with the exception that the PCB concentration for new oils should be zero.

Table 2-2: Recommended limits for oil properties of uninhibited regenerated oil (Dalton, 2008).

Oil	Unit	Specification	Reference and/or test method
Oil type		Naphthenic	Uninhibited
Colour	ISO units	≤ 1.0 max.	ASTM D1500
Appearance		Clear, free of sediment and suspended matter	IEC 60422
Density @ 20 °C	kg/dm^3	≤ 0,895 max.	ISO 3675/ISO 12185/ASTM D1298
Kinemetic viscosity @ 40 °C	mm^2/s	≤ 16,5 max.	ASTM D445/ISO 3104
Flash point	ºC	≥ 140 min.	ASTM D93/ISO 2719 (closed cup)
Aromatic content	%	6 to 14 max.	ASTM D2140/IEC 60590
Polyaromatic hydrocarbon	%	≤ 3,0 max.	BS2000 / IP 346
Neutralization value	mg KOH/g	≤ 0,03 max.	IEC 62021-1
Corrosive sulphur		Non-corrosive	IEC 62535
Moisture	mg/kg	≤ 10 max. (1) ≤ 20 max. (2). ≤ 10 max. (3)	IEC 60814 / ASTM D1533
Anti-oxidant additives	% by mass	No additives	IEC 60666
Oxidation stability acidity after 164 h @ 120 ºC	mg KOH/g	≤ 1.2 max.	IEC 61125 method C **
Oxidation stability sludge after 164 h@ 120 ºC	% by mass	≤ 0,8 max.	IEC 61125 method C **
Dielectric strength	kV/2,5 mm	≥ 70 min. (1) ≥ 60 min. (2)	IEC 60156
Polychlorinated biphenyl	mg/kg	≤ 20 max.	IEC 60619/EPA 600/ASTM D4059

(1) Prior to transportation
(2) On delivery
(3) Prior to filling

The process of oil regeneration typically follows PCB dechlorination to remove the products of oxidation and restore, where possible, the required physical and chemical characteristics of the oil. Uninhibited mineral oils depend on their natural inhibitors to retard oxidation while in use. The rate of inhibitor depletion is a direct function of the rate of oxidation which is determined by the oil temperature as well as the amount of oxygen, soluble contaminants and catalytic agents present in the oil. While oil regeneration processes restore most of the original oil characteristics and allows for reuse thereof, the natural inhibitor content cannot be replenished. In order for PCB dechlorinated oils to be reused in transformers their characteristics would need to conform to the limits set in Table 2-2.

2.4. THE EFFECTS OF OXIDATION ON MINERAL OIL CHARACTERISTICS

Mineral oil will undergo oxidation during operation. As mentioned in preceding subsections, the rate at which oxidation occurs is a direct function of the transformer operating temperature and the amounts of moisture (contained in the oil and solid paper insulation) and oxygen present within the transformer, which is intensified with the presence of electrical, mechanical and thermal stresses experienced during transformer operation as cited by Meshkatoddini (2008). During the oxidation process, chemically unstable intermediate compounds, namely free radicals, are produced resulting in the formation of organic acids and sludge (Dalton 2008). Webber (2006) cited that the purpose of the inhibitor, be it natural or artificial, is to scavenge these reactive free radicals and in so doing itself become a less reactive radical, thereby retarding the rate of oxidation. It is an accepted industry norm that the life expectancy of the mineral insulating oil is halved for every 10°C increase in mineral oil operating temperature. This norm is based on the understanding that the oxidation reaction rate is doubled for every 10°C increase in temperature. As shown by the oxidation mechanisms below, certain oxidation reactions can be initiated by the presence of high temperature only to produce a free radical that readily react with oxygen and moisture to continue the oxidation process (Nynas, 2001).

Oxidation mechanisms [14]:

1. Creation of a free radical (by heat, UV light or mechanical shear)

$$R\text{-}H \text{ ----> } R^* + H^*$$

2. Creation of peroxides by the reaction of the free radical with oxygen.

$$R^* + O_2 \text{ ----> } ROO^*$$

3. The peroxide may react and produce a new radical, alcohols, ketones, aldehydes and acids.

$$ROO^* + R\text{-}H \text{ ----> } ROOH + R^*$$
$$ROOH \text{ ----> } RO^* + HO^*$$

Where:

R-H = Hydrocarbon structure in present in the mineral oil

ROOH = Organic Acid

R*, H*, RO_2 *, RO*, HO* = Free radicals

At sufficiently high concentrations, the combined effects of oxidation products such as acid and sludge will have a damaging impact on a transformer in service (Meshkatoddini 2008). The acid present in the oil will initiate a chemical degradation reaction of the entire insulation systems (paper, pressboard & oil). Sludge accumulation on and between the windings and cooling surfaces of the transformer will in turn hamper its efficient cooling, causing further oxidation and resulting in the formation of more acid and sludge (Dalton 2008).

In his study Meshkatoddini (2008) uses oxidation degradation data from 43 transformers to validate the Arrhenius law and develop a natural logarithm to demonstrate the accelerated ageing of transformer oil under increasing temperatures.

$$t = A*e^{B/T}$$

Where,

t = Time

T = Temperature

A and B = Experimental constants based on the reacting materials, conditions and the system of units.

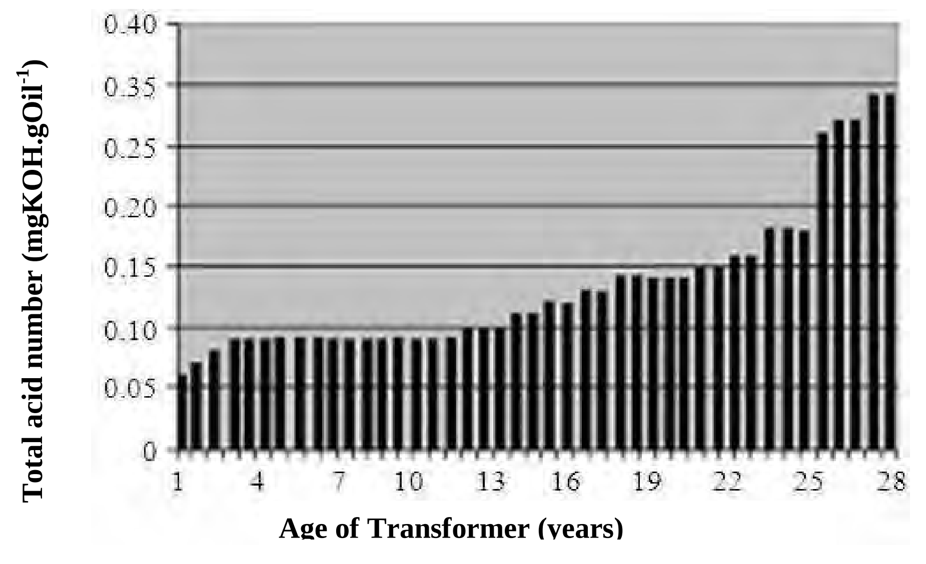


Figure 2-2: Acidity of the oil samples from 43 power transformers of various ages Meshkatoddini (2008)

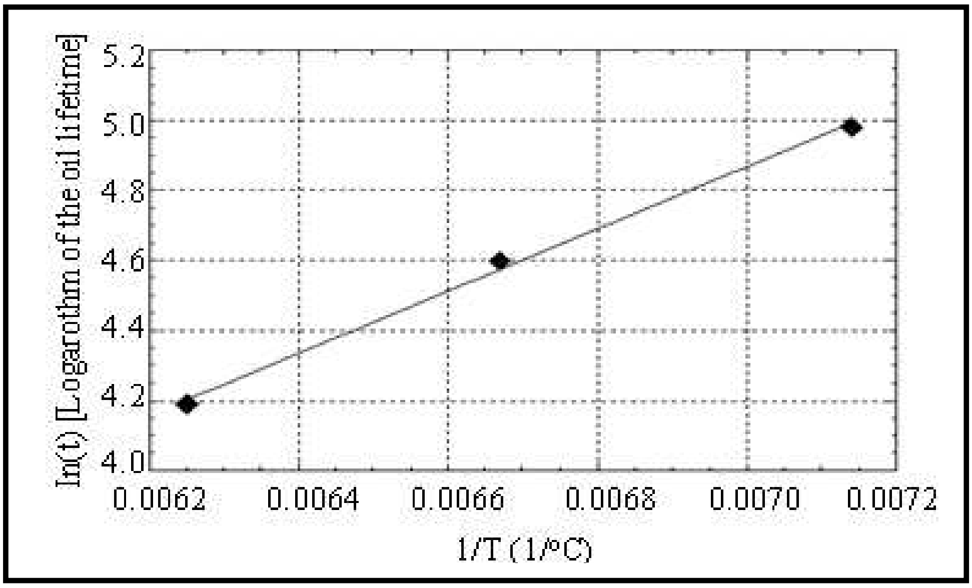


Figure 2-3: Arrhenius plot showing accelerated aging of an oil sample at different temperatures (Meshkatoddini, 2008).

From Figures 2-2 and 2-3 the increasing rate of mineral oil oxidation with increasing transformer operating temperatures can be inferred, which will be further expedited by the lowering of natural inhibitor of uninhibited mineral insulating.

2.4.1 OXIDATION EFFECTS ON DIELECTRIC STRENGTH

The oxidation process results in the formation of sludge, which as a suspended impurity and semi-conductive sediment, decreases the breakdown voltage of the mineral oil similar to that in the case of particles, and thereby decreasing the oil's ability to withstand electrical stresses (Dalton 2008: Nynas 2001).

2.4.2 OXIDATION EFFECTS ON NEUTRALISATION NUMBER

Acid is a by-product of oxidation and therefore, resulting in a directly proportional relationship between oil oxidation and the oil's neutralisation number is. The higher the rate of oxidation the higher the neutralisation number of the oil. (Dalton 2008: Nynas 2001).

2.4.3 OXIDATION EFFECTS ON MOISTURE CONTENT

Chemical degradation of the cellulose (paper & pressboard) results in the reduction of the cellulose chains also referred to as the degree of polymerisation, thereby reducing the insulating properties of the solid insulation. A by-product of the cellulose insulation degradation is the formation of moisture. Moisture in turn induces oxidation and will therefore partake in the further oxidation reactions and ultimately the production of more acid.

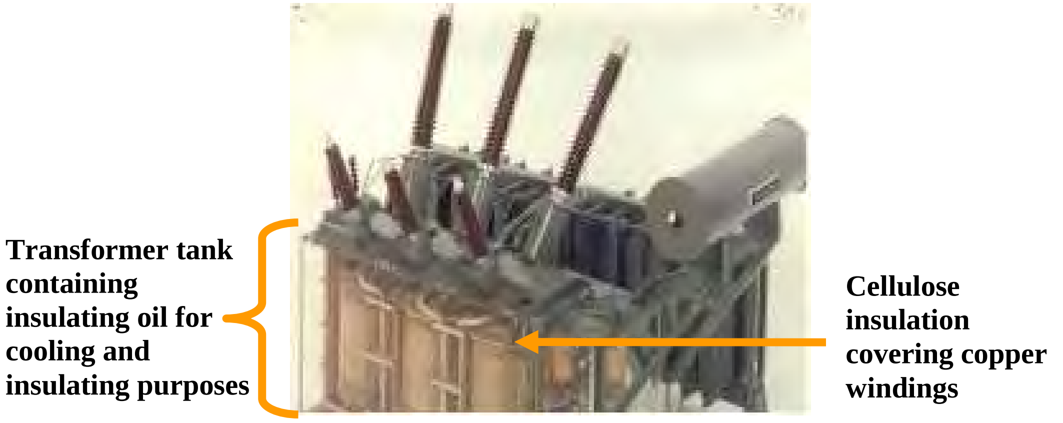


Figure 2-4: Transformer indicating the position of the paper insulation around the transformer windings

2.4.4 OXIDATION EFFECTS ON OXIDATION STABILITY

Oxidation stability is one of the most vital characteristics of insulating oil and provides an indication of the oil's resilience to oxidation processes. The oxidation stability of the oil is directly related to the inhibitor content of the oil and has an inversely proportional relationship with the rate of oxidation. If the oil has adequate inhibitor to retard the oxidation process then the oil will have good oxidation stability and vice versa (Dalton 2008: Nynas 2001)

2.4.5 OXIDATION EFFECTS ON PAH CONTENT

Lombard (1996) mentions the presence of two groups of polyaromatic hydrocarbons (PAHs) which are formed during the oil refining process of the mineral insulating oil. Lombard refers to the groups as "good PAHs" and "bad PAHs". The "good" PAHs add oxidation inhibiting characteristics to the oil through the production of phenols which are gas absorbing and acts as a free radical inhibitor. The "bad" PAHs have an oxidising effect on the mineral oil and a negative effect on the impulse breakdown of the oil. It is also stated in the literature that the "good gas absorbing PAHs" outweigh the amount of "bad oxidising PAHs" present in the oil (Lombard, 1996). It is not clear whether this is always the case. The overall effect of oxidation on the PAH content could thus be positive or negative depending on which of the PAH groups are dominant. The European Union and British Standards Institute have set the limit for total PAH concentration in mineral oil at 3%, for human health and environmental reasons.

2.4.6 OXIDATION EFFECTS ON TOTAL SULPHUR PERCENTAGE

The total percentage sulphur in mineral oil can be used to identify the oil type. Literature cited in this study indicates the presence of five types of sulphur present in mineral insulating oils, ranging from corrosive to very stable. Oxidation of the oil through degradation under optimal and stressed transformer operation results in the formation of acid. The test is performed via X-ray method, ISO14596, to measure total sulphur content.

2.5. CHARACTERISTICS OF PCBS

Polychlorinated Biphenyls are a group of synthetically produced non-polar compounds, each consisting of a biphenyl ring to which a maximum of ten chlorine atoms may be attached. This results in 209 possible PCB structures, commonly known as PCB congeners, having the generic chemical structure $C_{12}H_{10-x}Cl_x$, where x = 1-10, as described in the Encyclopedia of Environmental Sciences (Alexander *et al.*,1999).

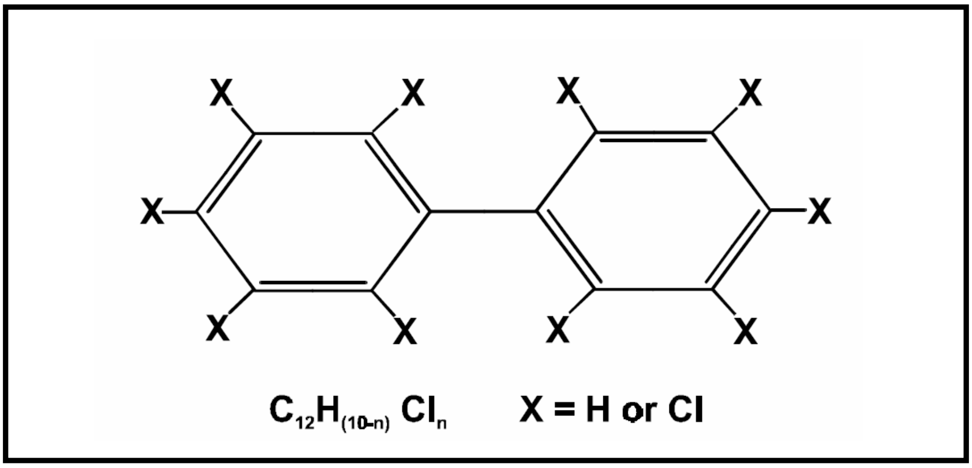


Figure 2-5: Generic molecular structure of PCB (UNEP Chemicals, 1999)

Sittig (1981), describes PCBs as non-volatile, chemically inert substances that only undergo reduction, oxidation, addition, elimination reactions under extreme conditions. While Erickson (1997) explains that individual PCB congeners are usually colourless and odourless crystals with specific properties depending on their chemical structures.

Table 2-3: List of PCB derivatives and their number of isomers (Erickson, 1997)

PCB Derivative	Number of Chlorine Atoms	Number of Congeners
Monochlorophenyl	1	3
Dichlorophenyl	2	12
Trichlorophenyl	3	24
Tetrachlorophenyl	4	42
Pentachlorophenyl	5	46
Hexachlorophenyl	6	42
Heptachlorophenyl	7	24
Octochlorophenyl	8	12
Nonachlorophenyl	9	3
Decachlorophenyl	10	1
Total Number of Congeners		**209**

A number of PCB congeners are combined with volumes of organic solvents (e.g. Trichlorobenzene) to produce complex commercial mixtures which are commonly referred to as Aroclors. Around ten different Aroclor mixtures, as listed in Table 2-4, were commercially produced under a range of trade names as contained in Table 2-5.

Table 2-4: Characteristics of Commercial Aroclors (Erickson, 1997)

Aroclor	Density @ 20^{o}C	Viscosity at 98.9 ^{o}C	Flash Point (^{o}C)	Distillation Range (^{o}C)	Solubility in water at 25 ^{o}C (µg/L)
1221	1.18	30-31	141-150	275-320	15000*
1232	1.26	31-32	152-154	270-325	1450*
1016	1.37	nv	170	323-356	420
1242	1.38	34-35	176-180	325-366	240
1248	1.44	36	193-196	340-375	52
1254	1.54	44-58	ntb	365-390	12
1260	1.62	72-78	ntb	385-420	3
1262	1.64	86-100	ntb	390-425	nv
1268	1.81	nv	ntb	435-450	nv
1270	1.95	nv	ntb	450-460	nv

ntb = None to boiling, nv = No value, * = Estimated

These Aroclors are identified in the environment by the number accompanying the term Aroclor i.e. Aroclor 1260, 1254, 1248, etc. Where “12 “represents the numbers of chlorine atoms within the biphenyl structure followed by the number representing the percentage Aroclor chlorination by weight (Erickson, 1997). The higher the percentage chlorination, the less volatile, more stable and therefore, the more bioaccumulative the Aroclor would be and vice versa. Appendix 1 of this dissertation contains the material safety data sheet (MSDS) for a broad range of Aroclors in oil.

Table 2-5: List of PCB Trade names (HSE , 2009)

PCB Trade Names				
Aceclor	Clophenharz	Elemex	No-flamol	Saf-T-Kuhl
Apriolio	Cloresil	Fenclor	Olex-SF-D	Santosol
Aroclor	Diaclor	Fenocloro	Orophene	Santhother
Asbestol	Delor	Gilotherm	Phenoclor	Sovol
Askarel	Delorene	Hyvol	Prodelec 3010	Sovtol
Auxol	DK	Inerteen	Pydraul	Terphenychlore
Aceclor	Dykanol	Kanechlor	Pyralene	Therminol
Chlorextol	Elaol	Kennechlor	Pyranol	Turbinol
Clophen	Electrophenyl	Leromoll	Pyroclor	

2.6. THE HISTORY OF PCBS

First synthesized in 1881, PCBs were considered ideal for a range of applications within various industries in open, partially open and closed applications. PCBs have been commercially produced since the late 1920’s in the United States (Pfafflin *et al.*, 2006). The Monsanto Chemical Company issued numerous trade licenses to chemical manufacturing companies across the globe, resulting in widespread production of PCBs under various trade names between 1930 and 1977. A survey of available non-incineration PCB destruction technologies (UNEP, 2002) estimated a world production of one million tons of PCBs between the 1930s and 1970s. Askarel being the most common mixture of PCBs found in equipment within Eskom. Until the 1960's knowledge relating to the toxicity of PCBs was limited within industry and not publicized. However, by 1972, sufficient scientific evidence existed to suggest that the toxic, persistent, and bio-accumulative properties of PCBs represented a serious hazard to human health and the environment, further discussed in section 2.7. In 1973, the Organization for Economic Co- operation and Development (OECD) instructed member countries to restrict PCBs to limited uses, as stated by Obaid *et al* (2003). PCB production ceased in the late 1970's after its toxic and bio-accumulative properties became known.

2.7. HEALTH & ENVIRONMENTAL IMPACTS OF PCB

Until the 1960's knowledge relating to the toxicity of PCBs was limited within industry and not publicized. However, by 1972, sufficient scientific evidence existed to suggest that the toxic, persistent, and bio-accumulative properties of PCBs represented a serious hazard to human health and the environment. In 1973, the Organization for Economic Co- operation and Development (OECD) instructed member countries to restrict PCBs to limited uses (Obaid *et al*., 2003). A collaborative study by the UNEP and the World Health Organization (1995) established the health impacts of PCBs described in the subsections below.

2.7.1 BIO-ACCUMULATION OF PCBS IN ORGANISMS

- PCBs are easily absorbed through the skin and through inhalation by both humans and animals and remain in the fatty tissue, where they tend to accumulate.

- More than 90% of ingested PCBs cross the intestinal walls and are retained in the organisms. The organ favoured by PCBs is the liver, which stores PCBs.

2.7.2 ACTUAL TOXICITY OF PCBS - POISONING OF HUMANS

Studies of cases of poisoning caused by accidental absorption of doses measuring 800 to 1000 mg/kg of PCB indicate that the first areas to show symptoms are the skin manifesting in itself in a condition called chloracne and in the eyes (oedema of the eyelids, watering of the eyes).

More general symptoms include liver disorders, bronchitis, certain peripheral neuropathies (tumours) and endocrine disruptions. These symptoms recede after approximately 1 year of continuous high level exposure. Abnormalities were observed in behavioural tests of children born to women who during pregnancy consumed PCB contaminated oil (Agency for Toxic

Substance and Disease Registry, 2001). These anomalies are primarily found on the skin, mucous membrane and the epidermis.

2.7.3 CARCINOGENICITY OF PCBS

Epidemiological studies have shown no significant increase in the incidence of cancer among individuals exposed to PCBs. Skin cancer, liver tumours and leukaemia have been attested, however scientific analyses have failed to establish a link between increased skin and pancreatic cancer rates and occupational exposure of the victims to PCBs.

The International Agency for Research on Cancer (IARC), which is part of the World Health Organisation (WHO), measures the carcinogenic risk of various chemicals and classifies them in two groups:

- Those which are “carcinogenic to humans” – group 1;
- Those which are “potentially carcinogenic to humans” – group 2.

Group 2 is further subdivided into groups A and B:

- For group 2A, evidence of carcinogenicity is “fairly well established”;
- For group 2B, evidence is “less well established”.

PCBs are classified as group 2B, i.e. potential human carcinogen.

2.8. PCB REGULATION IN SOUTH AFRICA

South Africa is a party to international agreements that impact on gradual phase-out and disposal of PCBs, namely the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention, 2001) and the Basel Convention on Transboundary Movement of Hazardous Waste and Their Disposal (1989).

2.8.1. STOCKHOLM CONVENTION

The Stockholm Convention is a global treaty aimed at eliminating specific Persistent Organic Pollutants (POPs) from use by specified dates as agreed to by the “Conference of Parties” (COP) on the convention. The convention was adopted on the 22nd of May 2001 in Stockholm, Sweden and was entered into force on the 17th of May 2004. South Africa ratified the agreement on the 4th of September 2004, as previously cited in chapter 1.

The Stockholm Convention outlines specific requirements with respect to the management of PCBs and its phase-out by 2025 and states that each party shall (Stockholm Convention 2001);

- “Make determined efforts to identify, label and remove from use equipment containing greater than 0.05 per cent polychlorinated biphenyls and volumes greater than 5 litres”;

- “Endeavour to identify and remove from use equipment containing greater than 0.005 percent polychlorinated biphenyls and volumes greater than 0.05 litres.” In accordance with subparagraph (e) of Annex A, Part II removal and elimination should be done by no later than 2028.

Appendix 2 of this dissertation contains a copy of Annex A, Part II of the Stockholm Convention relating specifically to the elimination of PCBs.

South Africa adopted the UNEP recommended PCB classification, which is based on classifications enforced within the United States and most European countries and inferred from the terms set under the Stockholm Convention. These classifications are as follows;

- PCB concentrations above 500 ppm are classified as pure PCB.
- PCB concentrations between 50 and 499 ppm are classified as PCB contaminated.
- PCB concentrations below 50 ppm are classified as PCB-free.

2.8.2 BASEL CONVENTION

The Basel Convention is a global treaty aimed at controlling the trans-boundary movement of hazardous waste and their disposal between countries. The need for this convention was identified in the late 1980’s when industrialised countries enforced stricter environmental regulations with costly penalties for transgressors, resulting in unscrupulous entities shipping their hazardous waste to developing countries.

The Basel Convention entered into force on the 5th of May 1992 with ratification by the South African Government on the 5th of May 1994. Parties to the convention are bound by a number of general obligations as listed in Article 4 of the agreement, with the main objective of protecting human health and the environmentally against the movement and disposal of hazardous materials (Basel Convention, 1992).

The convention accepts 50 ppm as the level above which PCBs are considered hazardous and recommends that all thermal processes that destroy PCBs have a DRE of 99.9999% and reduce PCB concentrations to below a scientifically-based minimum detection criterion as described in the PCB, PCT and PBB technical guidelines issued by the Basel Convention, (2003).

2.8.3 SOUTH AFRICAN LEGISLATION AND STANDARDS

The South African Department of Water Affairs classifies PCBs as hazardous in the national specification entitled "Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste" (1998). Based on this classification all national laws pertaining to the handling and disposal of hazardous waste are relevant in the management and disposal of PCBs. The relevant laws / acts are briefly described in subsection 2.8.3.1.

2.8.3.1 NATIONAL LEGISLATION RELATING TO THE MANAGEMENT PCBS

- South African Constitution (1996)

All persons have the right to an environment that is not harmful to their health and wellbeing and to an environment that is protected for current and future generations.

- Environmental Conservation Act (1989)

All waste disposal sites require the approval of the Minister of Water Affairs, including thermal and chemical treatment facilities.

- National Environmental Management Act (1998)

Owners of hazardous waste cannot transfer the liability to disposal contractors and shall remain liable for the safe management and disposal thereof inline with the "cradle to grave" philosophy. It is the responsibility of all individuals to ensure all reasonable and practical measures are taken when undertaking their activities to prevent harm to another person, their environment and/or property (Duty of Care).

- Hazardous Substances Act (1973)

The Act provides the regulations to manage and control the use of hazardous substances, and the disposal of hazardous waste within the country jurisdiction.

- National Environmental Management: Air Quality Act (2004)

Emissions generated by hazardous waste disposal processes must be in accordance with the national limits for stack emissions. PCBs shall not be disposed of in a manner that it causes air emissions in excess of the limits prescribed by the Act.

- Occupational Health and Safety Act (1993)

It is the duty of employers to inform, protect and train employees about the dangers of working with hazardous materials. It is the employee's responsibility to use all measures provided by the employer to protect himself/herself against any physical, mental or any other health impact that may arise from exposure to such hazardous material, such as PCBs, in the work environment.

- National Water Act (1998)

The Act makes provision for situations where pollution of water source may occur. No person shall intentionally pollute water sources, be it natural or unnatural, surface or ground water. Land owners and or persons occupying land shall take all reasonable measures to prevent the occurrence, continuation and recurrence of the pollution of water sources on or nearby the occupied land. PCBs shall therefore not be disposed of in a manner that it poses the risk of polluting water sources.

- National Road Traffic Act (1996)

The Act governs all vehicles, motorist, pedestrians, road planning, road quality, etc. The road transportation of hazardous substances such as PCBs require conformity with applicable road ordinances which is detailed in the SANS standards on transportation listed in Table 2-6.

- National Policy "Minimum Requirement for the Handling, Classification and Disposal of Hazardous Waste" (1998)

The policy provides a classification mechanism for both general and hazardous waste according to their inherent toxicological properties. Hazardous waste is given a rating based on the health and environmental risk they pose during disposal. PCBs are classified as a class 9 (Miscellaneous hazardous material).

2.8.3.2 National Standards

A list of national standards relating to the safe management, transportation and disposal of PCBs, thereby ensuring adherence to the national laws listed under subsection 2.7.3.2 are contained in table 2-6.

Table 2-6: SANS Documentation relating to the transportation of PCBs

Document Identification Number	Title of Document
SANS 290	Mineral Insulating Oils – Management and handling of Polychlorinated Biphenyls
SANS 555	National Standard for unused and reclaimed mineral insulating oils for transformers and switchgear
SANS 10228	The identification and classification of dangerous goods for transport
SANS 10229	Transport of dangerous goods - Purchasing and large packaging for road and rail transport
SANS 10231	Transport of dangerous goods - Operational requirements for road vehicles
SANS 10232	Transport of dangerous goods - Emergency information systems Part 1: Emergency information system for road transport

2.9. BASE CATALYSED DECHLORINATION FOR PCB DESTRUCTION

PCB base catalysed dechlorination processes are commercially available with some countries opting to reuse the dechlorinated oil as insulating and cooling media in their electrical equipment. The process is acknowledged and accepted by UNEP (Inventory of World-wide PCB Destruction Capacity, 1998) as an alternative non-thermal PCB destruction technology. The UNEP (1998) recommends utilisation of dechlorinated oils for functions, other than as insulating and cooling media in electrical equipment, such as in the production of lubricating oils, etc. The UNEP literature cited in section 2.9 of this dissertation does not clearly indicate whether the reuse of dechlorinated oils in electrical equipment is supported but it does warn of potential effects on artificial inhibitors contained in inhibited mineral oil as a result of the dechlorination process. The decision to use dechlorinated oils as insulating and cooling media in electrical equipment, such as transformers, therefore reside with the utility and should be based on sound strategic, environmental and economic considerations.

A range of processes are commercially available for dechlorination of PCB contaminated oils. The operating principles for most of the commercially available dechlorinators are similar but they utilise different proprietary reagents to achieve dechlorination. A market evaluation undertaken by Nassiep (2005) describes the technical, economic and safety considerations for a number of commercially available PCB dechlorination technologies. Variations of the technology utilise sodium, potassium or glycol mixtures combined with proprietary reagents to effect dechlorination of PCBs in mineral oil.

2.9.1 PRINCIPLE OF OPERATION

Dechlorination processes involve the addition of an alkali or alkaline earth metal carbonate, hydroxide or bicarbonate to the contaminated medium, thereby replacing the chlorine atoms on the PCB molecules with hydrogen.

Parker *et al.*(1981) describes the typical processes incorporating an alkali metal, such as the process used in the experimental part of this study uses a alkali metal dispersion (sodium) to which an aromatic radical anion substrate (naphthalide) is added in the presence of an ether-type solvent (tetrahydrofuran) to produce an alkali metal aromatic radical anion reagent (sodium naphthalenide). The reagent is added to the PCB contaminated oil to bring about a reaction with the chlorine atoms attached to the PCB. The chlorine content is converted to inorganic salts and the chlorine-free polymeric structures (or biphenyls) fraction is removed by organic fraction filtration or centrifugation. Reactions take place under inert atmosphere, so as to avoid the risk of an explosion or fire, and in the absence of water as wastes are pre-dried by heating. The plant can be either fixed or mobile, and used on PCB within an operating transformer with the process taking up to a week.

2.9.2 REACTION KINETICS OF SODIUM DISPERSION DECHLORINATION

Huang *et al.* (2007) conducted laboratory scale experiments using a laboratory scale reactor to determine the reaction kinetics of the sodium dispersion dechlorination process by means of single particle evaluation. The sodium metal dispersion was allowed to react with a mixture of PCBs and mineral insulating oil under varying experimental conditions, so as to simulate a full scale process.

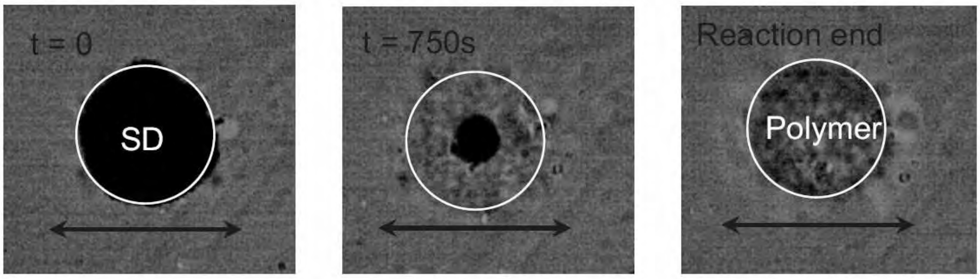


Figure 2-6: Visuals of PCB-sodium dispersion single particle reaction (Huang *et al.,* 2007)

The black dot in the first photograph of Figure 2-5 is the sodium dispersion as seen at time (t) = 0 i.e. before the reaction commences. It is evident that with time the dot becomes smaller from the outside in, indicating a surface reaction between the PCBs and the sodium dispersion. In the third visual the dispersion is completely replaced by a polymeric structure.

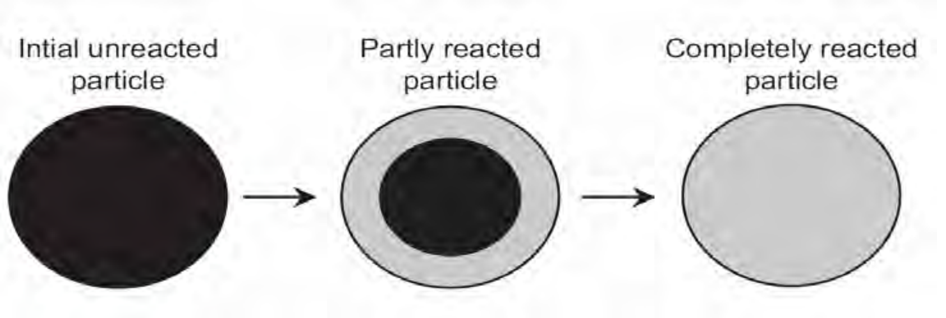


Figure 2-7: Simulated sodium-PCB reaction model (Huang *et al.,* 2007)

From the photographs it is inferred that the reaction occurs in three steps, namely;
Step 1: Chemical reaction between the PCB and the sodium particle at interface.
Step 2: Diffusion of the PCB through the polymer layer generated by the reaction.
Step 3: Reaction of PCBs with the sodium dispersion after penetration through the polymer layer.

The dechlorination reaction can be derived through utilisation of the shrinking core model (SCM) as defined by Lievenspiel *et al.*(1999).

$$X_B = \frac{C_{\mathrm{sod}}(4\pi/3)(R^3 - r^3)}{C_{\mathrm{sod}}(4\pi/3)R^3} = 1 - \left(\frac{r}{R}\right)^3.$$ (Huang *et al.*, 2007).

Where:

XB = Fractional conversion of SD particles (dimensionless)
Csod = Sodium concentration (mol.m^{-3})
R = Initial radius of SD particle (m)
r = Radius of SD particles (m)

The reaction rate for the sodium dispersion – PCB reaction was derived using the SCM with data incorporated from the laboratory sodium dispersion and PCB experiment. The reaction rate was then expressed as follow:

$$\begin{aligned}\gamma &= C_{\mathrm{sod}} \cdot \frac{4}{3}\pi R^3 \cdot \frac{\mathrm{d}X_B}{\mathrm{d}\tau}\\ &= \frac{4\pi R^2 C_{\mathrm{PCBs}}}{\frac{1}{D_{eA}/R}[(1-X_B)^{-1/3}+1] + \frac{1}{\kappa_c}(1-X_B)^{-2/3}},\end{aligned}$$

$$\kappa_c = 5.13 \times 10^{-18} \exp\left(-\frac{7096.58}{R_g T}\right),$$

$$D_{eA} = 2.35 \times 10^{-23} \exp\left(-\frac{17131.47}{R_g T}\right),$$

(Huang *et al.*, 2007)

Where:

XB = Fractional conversion of SD particles (dimensionless)

*C*PCB = PCB concentration *(*mol.m−3*)*

*C*sod = Sodium concentration (mol.m^{-3})

R = Initial radius of SD particle (m)

DeA = Effective diffusion coefficient *(*m^{2}.s^{-1}*)*

kc = Rate constant *(*ms^{-1}*)*

Rg = Gas constant *(*8.314 J.mol^{-1}K^{-1}*)*

T = Reaction temperature (K)

γ = General reaction rate *(*mol.s−1*)*

τ = Reaction time (s)

The derived model was tested for verification by comparing experimental data with theoretical data obtained from the reaction model through a experimental simulation of PCB: Na at 10 %wt and a reaction temperature of 160°C. Table 2-7 contain the additional reaction conditions and constants for the experiment.

Table 2-7: Condition and constants for the simulated reaction (Huang *et al.*, 2007)

Measure	Unit of Measurement	Value
Concentration of PCB	wt %	10
Na : Cl	ratio (dimensionless)	1
Density of Na	$g.cm^{-1}$	0.97
Density of PCB	$g.cm^{-1}$	1.376
Density of Oil	$g.cm^{-1}$	0.88
Density of Polymer	$g.cm^{-1}$	1.581
*Q*exo	$kJ.g^{-1}$	4.61
K_{Na}	$kJ.kg^{-1}K^{-1}$	1.23
K_{pol}	$kJ.kg^{-1}K^{-1}$	0.984
K_{oil}	$kJ.kg^{-1}K^{-1}$	2.1
K_{PCB} (biphenyl tetrachloride)	$kJ.kg^{-1}K^{-1}$	1.54

The good comparison was observed between the experimentally obtained data when compared with the data derived through the model.

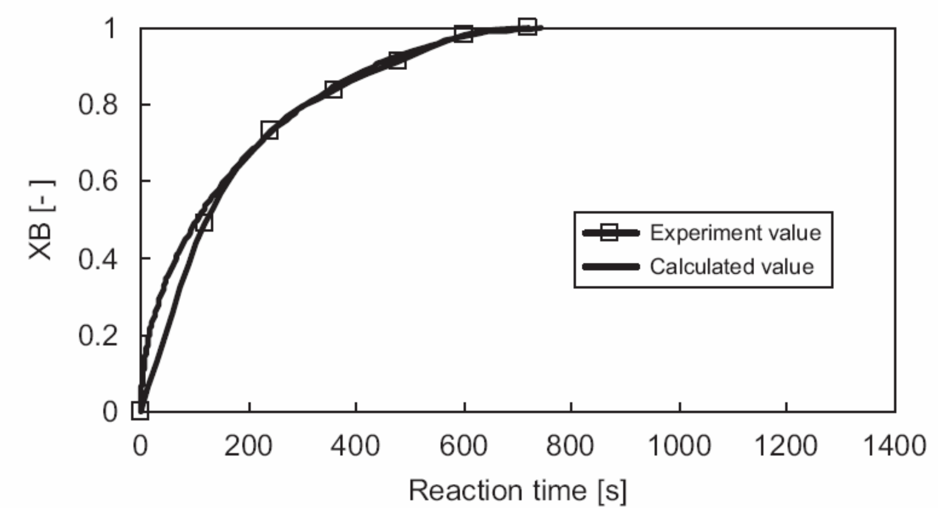


Figure 2-8: Model regressed by Huang et al. (2007) to the reaction rate, based on 10%wt PCB at 160°C.

The study also established the ideal particle size by comparing the reaction rate of particles between 5µm and 10µm in size. Figure 2-8 shows effect of the sodium dispersion particle size on the time taken to complete the dechlorination reaction.

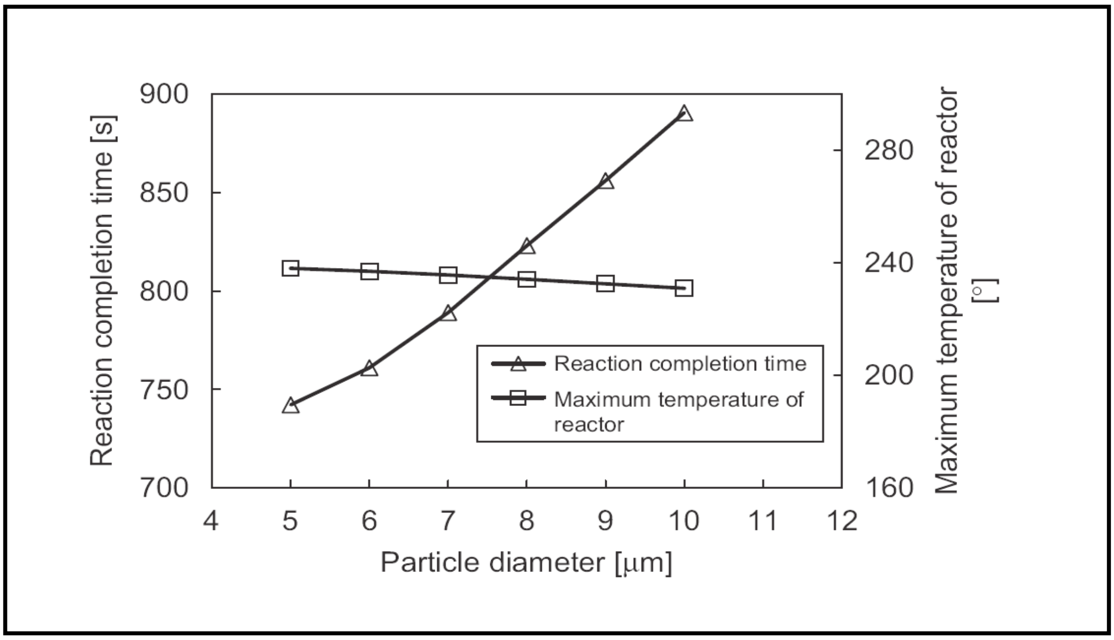


Figure 2-9: Sodium dispersion particle size vs. reaction time (Huang *et al,* 2007).

The results obtained from the reactions depicted in Figure 2-8 indicate a directly proportional relationship between the sodium dispersion particle size and the time taken to complete the reaction. This result is expected, according to the author of this dissertation, as the reaction would be completed faster as the particle size is reduced. The study makes the following assumptions:

- That all particles within the sodium dispersion are of the same size, surface areas and that all the sodium particles present will react at the same rate.
- That the density distribution of PCBs and sodium dispersion is the same.
- That pseudo-steady-state in which PCBs react with sodium dispersion particles in the following manner only;

nPCB(C12H6C14) + 4nNa → Polymer([C12H6]n) + 4nNaCl……………(1)

It is the view of the author of this dissertation that the reaction rates depicted in Figure 2-8 are idealistic and void of a number of variables such as the particle size distribution of the sodium dispersion, and the presence of unknown catalysts which may be present during the actual commercial scale sodium dechlorination reaction chamber.

2.9.3 EFFECTS OF SODIUM BASED DECHLORINATION ON MINERAL INSULATING OIL

The effects of PCB dechlorination on uninhibited mineral oils are not well documented. A study undertaken by Pahlavanpour *et al.*(1992) cites two major concerns relating to the sodium based PCB dechlorination processes. These concerns relate to the safety of the system, due to the use of highly reactive sodium metal dispersions and the risk of explosion in the presence of excess oxygen and moisture. The second concern cited refers to the reduction in natural inhibitor content of uninhibited mineral oil after sodium dechlorination. These concerns were mentioned as the basis for the undertaken of a study on a non-sodium based dechlorination technology namely PCB Gone and did not provide a reference or any additional information relating to the sodium study. The UNEP (Inventory of World-wide PCB Destruction Capacity, 1998) cited a possible disadvantage relating to the sodium dechlorination is that the process may destroy oxidation inhibitors. Very limited information is available on the effects of dechlorination on natural inhibitors of uninhibited mineral oil and no information is available which quantifies the effects associated with the reuse of uninhibited dechlorinated oils in transformers.

2.10 OTHER PCB DESTRUCTION TECHNOLOGIES

All PCB destruction technologies operate on the premise of destruction of molecular bonds by use of chemical, physical or microbial means. The UNEP, in its inventory of world-wide PCB destruction capacity report (1998), explains that one way in which to characterise thermal PCB destruction technologies is through its Destruction and Removal Efficiency (DRE) percentage. It is important to note that the DRE of a particular PCB destruction technology is a calculated value based on gravimetric analysis principles and should not be confused with the analytical capabilities of PCB analysis and detection instrumentation such as Gas Chromatography or Gas Chromatography – Mass Spectroscopy.

$$\left(\boldsymbol{DRE} = \frac{\boldsymbol{W}_{in} - \boldsymbol{W}_{out}}{\boldsymbol{W}_{in}} \quad \text{X} \quad 100 \right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

(UNEP, 1998)

Where:

$\boldsymbol{W}$in = mass feed rate
$\boldsymbol{W}$ out = mass emission rate

The DRE rating of a thermal destruction technology is a calculated percentage that represents the number of molecules of a compound removed or destroyed by a thermal destruction technology relative to the number of molecules entering the system. The DRE calculation measures only the mass of the compound in the emissions whereas the destruction efficiency (DE) of a technology measures the mass of the compound in gaseous emission aqeous and solid residues relative to the mass (number of moles) entering the system. (UNEP, 1998)

Nassiep (2001) cited the following available PCB destruction technologies during an investigation of commercially available and emerging thermal and non-thermal processes for PCB destruction:

- High temperature incineration
- Encapsulation & landfilling (non-destruction – long term storage)
- Plasma treatment
- Ozonation
- Ball milling
- Cement kilns (for incineration)
- Eco Logic
- Supercritical water oxidation
- Solvated electron technology
- Molten salt
- Thermal desorption & oxidation

2.10.1 HIGH TEMPERATURE INCINERATION

PCBs have been disposed of primarily through high temperature oxidation, i.e. incineration. The PCB compound is converted to amongst other hydrochloric acid and water at temperatures above 1350°C. However, a risk exists of formation of by-products produced at temperature below 1350°C, which are of major health and environmental concern. These by-products such gaseous dioxins and furans are referred to as “Products of Incomplete Combustion” (PICs). Hazardous waste incinerators have varied designed and typically comprise rotary kilns, combustion chambers and adequate afterburners and scrubber (filtration) systems to minimise the risk of dioxin and furans being released to atmosphere (Rahuman *et al.*, 2000).

The technology, if properly operated, is highly effective in the destruction of PCBs with reported DREs of 99,9999%. Environmental concerns relating to the inherent threat of toxic emissions renders this method of destruction less environmentally sound. This could however be overcome by the dilution of the PCB oil to non-PCB contaminated heavy furnace fuel (HFO) or non-PCB contaminated waste oil prior to incineration to assist in the reduction of toxic emissions such as dioxins and furans.

2.10.2 ENCAPSULATION & LANDFILLING

Encapsulation and landfilling of hazardous waste is a disposal method in which materials are buried between multiple layers of low and high permeability soil and low permeability geo-synthetic substances to prevent contact with the environment and ground water systems. PCB contaminated oil are placed in metal containers and then buried to ensure effective containment. The process does not involve destruction of the compounds *per se* but, rather long term storage. The landfill sites needs to be continuously maintained and monitored to ensure containment of the hazardous material so as to prevent potential damage, due to leakages into the environment. A major setback to this disposal option is that waste owners remain liable for any environmental damage that may occur as a result of landfill leakages (National Environmental Management Act, 1998).

2.10.3 PLASMA TREATMENT

The process involves the direct injection of a liquid or gaseous hazardous waste stream with inert argon gas into a plasma arc which provides plasma temperatures in excess of 3000^{O}C resulting in pyrolysis of the hazardous waste. This means that the organic materials contained in the waste dissociates into elemental ions and atoms in the absence of oxygen. The elemental ions and atoms recombine in the cooler area of the equipment's reaction chamber prior to a rapid alkaline quenching step to form simple non-hazardous molecules. The end products of the process are argon gas, carbon dioxide, water vapour and an aqueous solution of inorganic salts. The destruction and removal efficiency (DRE) of organic compounds is greater than 99.99% (CMPS&F, 1997).

Plasma treatment has also been applied to solid hazardous waste streams through the Plasma Arc Centrifugal Treatment (PACT) process. The plasma torch heat is used to melt and vitrify solid waste feed material resulting in vaporisation, decomposition and ionization by the air used as plasma gas. This is followed by an off-gas treatment system. Solid are vitrified into a monolithic non-leachable mass. PACT has a DRE of 99.996% (CMPS&F, 1997).

2.10.5 OZONATION

Ozone is generally used for odour removal and disinfection of various water streams. The process has been successfully applied to PCBs contained in oil and soil to form carbon dioxide, water and hydrochloric acid via the formation of free radicals that degrade ozone in different media. The DE for ozonation is 93% (Nassiep, 2001).

2.10.6 BALL MILLING

Ball Milling is a mechano-chemical process that uses the energy produced and released form collision between balls in a ball mill. The energy is used to activate a reaction between the lime and hazardous waste resulting in the degradation of organo-chlorine waste compounds. The process has been successfully used to decontaminate solid PCB waste streams. The process forms low toxicity products, amongst which are graphite, calcium chloride and calcium hydroxide. No gaseous emissions are produced by the process (CMPS&F, 1997)..

2.10.7 CEMENT KILNS

The use of cement kilns for PCB disposal has been widely used in Europe. The cement manufacturing process requires the use of large quantities of raw materials and the kilns require operating temperatures inline with those required for the destruction of PCB. PCB contaminated waste can be fed directly into the middle of the kiln via a hopper or the waste can be pre-treated through a thermal desorption (volatilisation and extraction) of PCB from the solid media prior to treatment / use as feed in the kiln (Rahuman *et al.*, 2000). Temperatures in >2000^{O}C and long retention times for both gases and raw materials make this method of destruction effective for the destruction of PCBs (CMPS&F, 1997). The process would however require stricter emissions monitoring to ensure dioxins and furan levels are within South African stack emission limits (Nassiep, 2001). Dioxin and furan monitoring and analysis are currently extremely costly, which may be a deterrent in the local application of this disposal option.

2.10.8 ECO LOGIC

This patented process relies on the gas phase thermo-chemical reaction of hydrogen with organic compounds, i.e. thermal hydrogenation. At temperatures above 850^{O}C hydrogen combines with organic compounds in a reduction reaction forming shorter chained hydrocarbons (primarily methane) and hydrogen chloride. The reaction is enhanced by the presence of water, which acts as a reducing agent and hydrogen source. The average DRE of the Eco Logic process during independent evaluations undertaken between 1995 and 1996 was 99.999995% (CMPS&F, 1997).

2.10.9 SUPERCRITICAL WATER OXIDATION (SCWO)

SCWO is a high temperature and pressure technology that incorporates the properties of supercritical water in the destruction of organic compounds and toxic waste.

The process decomposes PCB by using an oxidising agent (typically oxygen or hydrogen peroxide) and the solubility properties of supercritical water having a temperature of $\geq 374^{O}C$. The reaction occurs in a homogenous phase where carbon is converted to carbon dioxide, hydrogen to water and chlorine (derived from organo-chlorine compounds) to chloride ions. The reactions are exothermic and the process is self sustaining at appropriate concentrations of organic waste. The process produces disposable ash, salt solutions and non-toxic gases. SCWO has a DRE of >99.99994% for dioxins (Rahuman *et al.*, 2000: Nassiep, 2001: CMPS&F, 1997).

2.10.10 SOLVATED ELECTRON TECHNOLOGY

The process uses a proprietary reagent namely Agent 313 for the treatment of PCB contaminated waste streams. Solvated electrons are extremely powerful reducing agents (Nassiep, 2001).

An alkali metal (sodium, calcium or lithium) is dissolved into anhydrous ammonia turning the solution bright blue as electrons are freed. Free radical electrons are strongly attracted by halogenated compounds and when mixed with the solvated solution become instantaneously neutralized. During the treatment of PCBs, chlorine combines with the ions of sodium to form sodium chloride, biphenyls and an uncontaminated media (oil, soil, etc.) as described by Rahuman *et al.* (2000).

2.10.11 MOLTEN SALT

The process involves the use of a molten alkaline salt bed, typically sodium carbonate, which oxidises organic materials at temperatures between $900^{O}C$ to $1000\ ^{O}C$. The chlorine contained in the organic feed is retained in the molten salt bed. The process achieved DREs of 99.9999970% ($900^{O}C$) and 99.9999932% ($1000\ ^{O}C$) for trichlorobenzene and >99.9999988% during treatment of chlordane.

2.10.12 THERMAL DESORPTION AND OXIDATION

The process comprises a combination of a pre-treatment technology known as thermal desorption followed by thermal oxidation and final volatile organic compounds (VOC) destruction.

Thermal desorption is a physical separation process which is not necessarily designed to destroy organics. Contaminated waste is heated to volatilise water and organic contaminants and due to the high temperatures organic compounds become decomposed. The volatilised material is vacuum drawn and destroyed in an after-burner. The use of the thermal desorption step allows for only the volatiles to be destroyed in the afterburner and not the entire mass of material, as in the case of conventional PCB incineration.

In the case of PCB oils, the materials are heated in a horizontal rotary kiln, which consists of an inclined rotating tube so that the waste moves horizontally as well as radially through the kiln. In the case of capacitors, these are first stripped and drained under vacuum prior to treatment. Depending on the percentage chlorination, PCBs are fed into the kiln at a rate of around 200 kg/hour. The kiln is operated at temperatures above 600^{o}C allowing for the flashing off of the hydrocarbons. The gases released are then exposed to an oxidative atmosphere at temperatures above 1350^{O}C for a period of >2 seconds in the presence of a proprietary reagent. The after-burner converts volatile organic compounds (VOCs) and other gaseous hydrocarbon pollutants to carbon dioxide, water and inorganic salts. The afterburner is followed by a rapid gas-quenching step minimising the potential for dioxin formation. A gas clean-up plant consisting of a scrubber and a packed column (dry gas collection filter unit) follows the quenching step. The gas clean-up plant neutralises acid gas and reduces particulates, halides, heavy metal and other unwanted pollutants to the required emission levels. The plant has online gas and pH monitors. Solid residues are tested for the presence of PCBs and PAHs prior to disposal in a general waste landfill site.

2.11 INSULATING OIL REGENERATION

Insulating oil regeneration, also referred to as insulating oil reclamation, can be defined as a process whereby contaminants such as acids, water, impurities and suspended solids of used oil is removed by chemical or adsorbent means so as to restore the oil characteristics similar to those of new insulating oil. Commercially available regeneration plants use Alumina or Fuller’s earth (Pahlavanpour *et al.*, 1994) for the removal of oil oxidation products.

The process involves the purification and subsequent percolation of the oil through a set of columns containing the Fuller's earth adsorptive medium. Figure 2-9 provide an overview of the typical oil regeneration plant.

The oxidised oil enters the system and is heated and kept at a temperature between 65 -70°C, by a set of electric heaters. The oil then passes through a set of coarse filters to remove suspended solids and excess moisture. This is followed by forced percolation of the oil through the adsorptive clay bed consisting of a range of columns containing Fuller's earth clay, at a temperature of 65°C. The oil leaving the columns is pumped through a fine filter (typically 0.5 micron rated filter) before being degassed in the vacuum chamber. The process removes acids, sludge, polar compounds and suspended impurities and regenerates the insulating properties of the mineral oil to allow for its reuse in electrical equipment. The study undertaken by Phalavanpour *et al (1994)* established that the regeneration process did not remove the natural inhibitor from the oil.

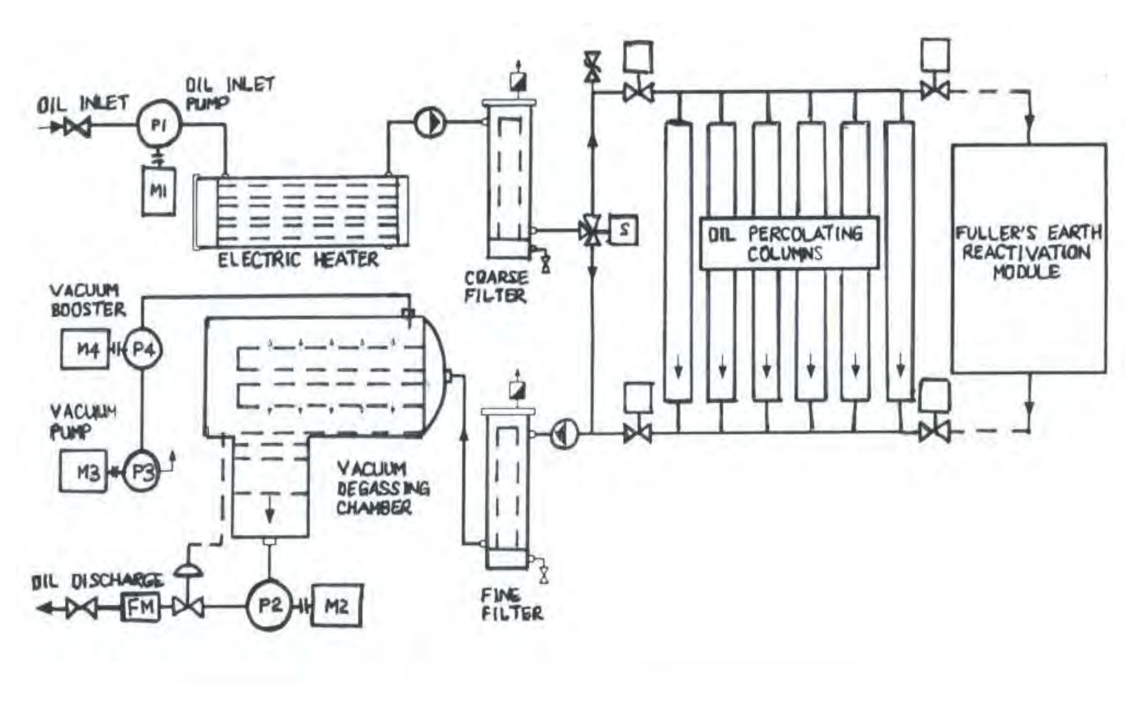


Figure 2-10: Schematic of the Fuller's earth oil regeneration process (Pahlavanpour *et al.*1994).

2.12 ARTIFICIAL NEURAL NETWORKS

Artificial neural networks, commonly known as neural networks are cited by Hagan *et al.* (1999) as computationally intelligent models that have the ability to learn and are considered to be the computational equivalent of the human brain. They were first introduced in the 1940's and have been used in applications such as self driven cars, pattern recognition, stock market prediction, AIDS modelling to mention a few. The neural networks subject is broad and makes use of optimisation techniques, statistical methods, numerical methods etc., most of which are beyond the scope of this study.

This section provides an overview of neural networks, their application to model the process of dechlorination and the 164 hour oxidation test used during this study. The multilayer perceptron neural network is introduced together with its application in process modelling. Also presented is the backpropagation algorithm, one of the most efficient procedures to train multilayer perceptron neural networks.

2.12.1 NEURAL NETWORK FUNDAMENTALS

As seen in Figure 2-11, there is some actual physical process to be modelled. The objective is to adjust the parameters of the neural network so that it will produce the same output as the actual process. The input x to the actual process, whatever it may be, is applied to the process. The resulting output is the actual or target output t, which is produced by the process. When x is applied to the neural network, the network output y must be approximately equal to the target output t. If they are not equal, then the difference (y-t) is computed as seen by the summation symbol. This difference is fed back into the network so as to alter the parameters such as weights and biases so that the network output y equals the target output t. This is known as training the neural network to model some process.

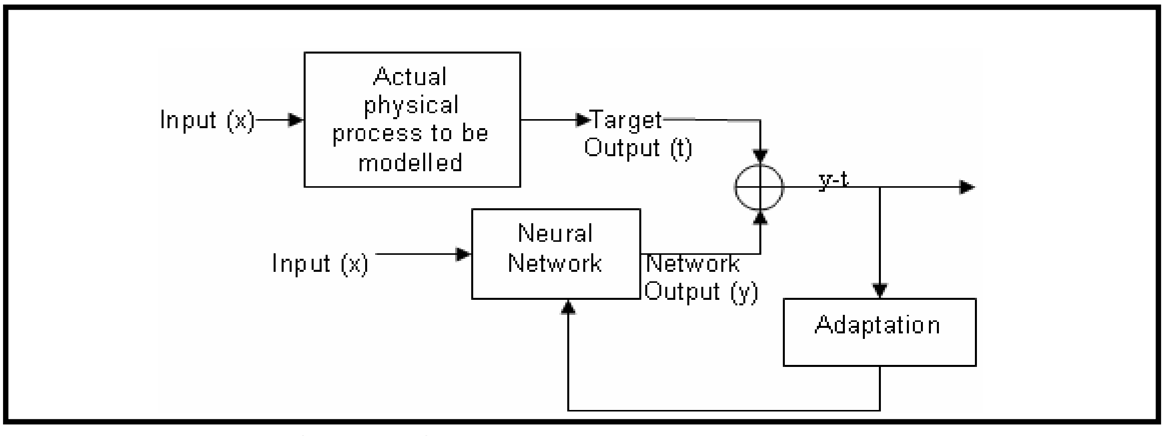


Figure 2-11: System configuration for developing (training) and testing a neural network

2.12.2 MULTILAYER PERCEPTRON NEURAL NETWORK

An example of a multilayer perceptron neural network is seen in Figure 2-12. This is a two layer network.

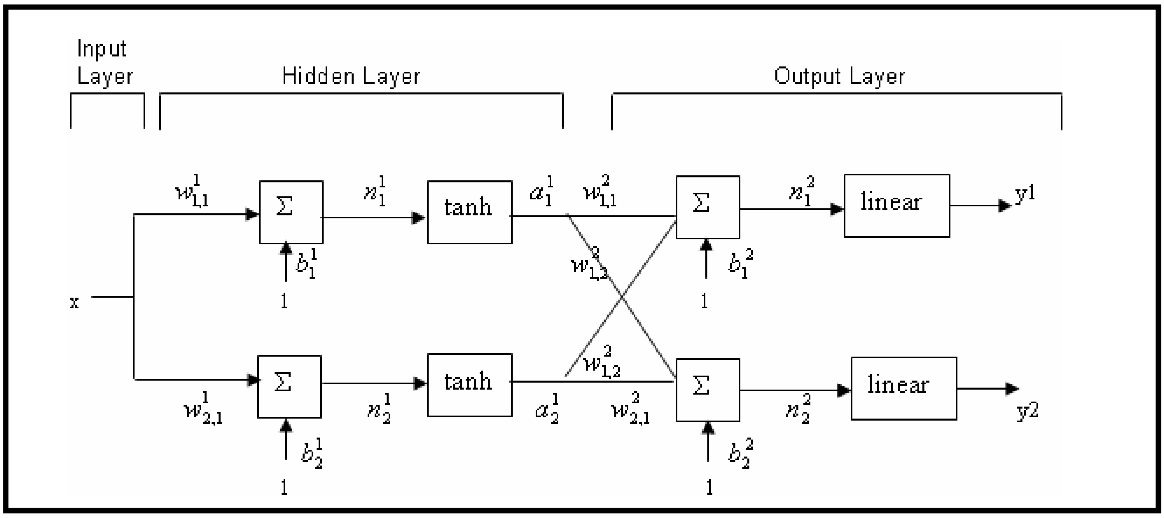


Figure 2-12: A two layer perceptron neural network with two neurons in the hidden layer and 2 neurons in the output layer (Hagan, 1999)

Each layer has its own weight matrix **w**, its own bias vector **b** and a net input vector **n** (Hagan *et al.,*1999). In the first layer the single input **x** is multiplied by the weight matrix **w** to form **wx** which is sent to the summer. The other input, 1, is multiplied by **b** and is also sent to the summer. The output of the summer **n** is called the net input. This is sent to the activation function (hyperbolic tangent in the hidden layer and linear in the output layer) to produce the outputs **a** in the first layer and **y** in the second. **w** and **b** are parameters which are adjusted by a learning rule until the neural network models the specified process (Hagan *et al.*,1999). The activation function is chosen according to the application or the process being modelled. Each activation function pair is called a neuron.

Two layer neural networks with a Log-Sigmoid activation function in the first layer and a linear activation function in the second are known as universal approximators. These universal approximators are able to model almost any process or system given the right circumstances. Using a hyperbolic tangent function in the first layer also makes for a good approximator. The equations that govern the neural network in Figure 2-12 are below.

$n_1^1 = w_{1,1}^1 \mathrm{x1} + b_1^1$ and $n_2^1 = w_{2,1}^1 \mathrm{x1} + b_2^1$ …………………………………………………….(3)

$a_1^1 = \tanh(n_1^1) = \tanh(w_{1,1}^1 \mathrm{x1} + b_1^1)$ and $a_2^1 = \tanh(n_2^1) = \tanh(w_{2,1}^1 \mathrm{x1} + b_2^1)$………………(4)

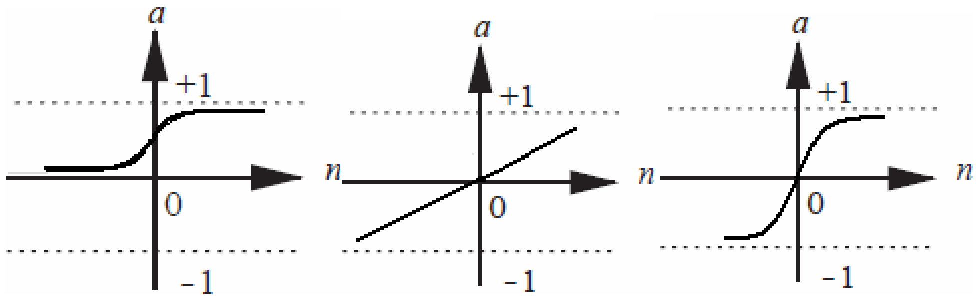
$n_1^2 = a_1^1 w_{1,1}^2 + a_2^1 w_{1,2}^2 + b_1^2 = \tanh(w_{1,1}^1 \mathrm{x1} + b_1^1) w_{1,1}^2 + \tanh(w_{2,1}^1 \mathrm{x1} + b_2^1) w_{1,2}^2 + b_1^2$ …....(5)

y1 = lin(n_1^2**) = lin(tanh(**$w_{1,1}^1$ **x1 +** b_1^1**)** $w_{1,1}^2$ **+ tanh(**$w_{2,1}^1$**x1 +** b_2^1**)** $w_{1,2}^2$ **+** b_1^2**)**……………….(6)

$n_2^2 = a_1^1 w_{1,2}^2 + a_2^1 w_{2,1}^2 + b_2^2 = \tanh(w_{1,1}^1 \mathrm{x1} + b_1^1) w_{1,2}^2 + \tanh(w_{2,1}^1 \mathrm{x1} + b_2^1) w_{2,1}^2 + b_2^2$……(7)

y2 = lin(n_2^2**) = lin(tanh(**$w_{1,1}^1$ **x1 +** b_1^1**)** $w_{1,2}^2$ **+ tanh(**$w_{2,1}^1$**x1 +** b_2^1**)** $w_{2,1}^2$ **+** b_2^2**)**………………..(8)

The graphs of the various activation functions discussed are seen in Figure 2-11.



a = logsig(n)   a = lin(n)   a = tanh(n)

Figure 2-13: Log-sigmoid, linear and hyperbolic tangent activation functions

2.12.3 TRAINING THE NEURAL NETWORK

In this section the method of determining the neural network parameters, weights and biases, or training the neural network is presented. A common and effective training method based on a quasi-Newton optimization algorithm known as backpropagation is used. The method is termed backpropagation because derivatives are processed from the first layer of the network to the last. A comprehensive reference for alternative algorithms to quasi-Newton optimization is discussed by Hagan *et al.* (1999). The following equations are used to determine the weights and biases. The derivations of the above equations are beyond the scope of this research and can be found in (Hagan *et al.*,1999).

$$[W_{n+1}] \approx [W_n] - \alpha \left[\frac{\partial E}{\partial W_n} \right]$$ and

$$[b_{n+1}] \approx [b_n] - \alpha \left[\frac{\partial E}{\partial b_n} \right] \quad \ldots\ldots(9)$$

α is known as the learning rate. The *E* in the partial derivatives seen above represents the mean square error performance index, which is found as follows.

$$E \approx \sum_{j \approx 1}^{M} \sum_{i \approx 1}^{N} (y-t)^2 + \alpha(\sum W^2) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where y = f(W, x), M is the number of training samples, N is the number of outputs and f represents the activation function of a layer in the neural network. The second term in (10) above makes sure that the orders of magnitudes of all weights are the same.

The first step in training the neural network is to initialize the weights and biases with random values. The input x is then applied to the neural network and is processed through equations (3) to (8) to produce the network output y. The difference between network output y and the target output t (i.e. the output from the actual process) or the error is found using equation (10). This error is used to find the next set of values of the weights and biases from equation (9). This is called a training cycle. The next training cycle then begins whereby once again the input x is applied to the neural network which now has new values for the weights and biases found during the first training cycle. After the second training cycle the error from equation (10) would have decreased. In this manner the neural network goes through many training cycles until the error is sufficiently small.

One method to determine the number of neuron as well as the number of training cycles is called Early Stopping, of which a detailed explanation is given by Hagan *et al.* (1999). The number of layers is determined depending on the complexity of the process being modelled however 2 layers suffice for most applications.

2.13 SUMMARY OF LITERATURE REVIEWED

The key findings of the literature reviewed in this chapter are summarised as follows:

- Uninhibited naphthenic based mineral oil contains natural inhibitors such as certain of the sulphur, aromatic and nitrogen based compounds present in the oil.

- Mineral oil serves two main functions in transformers namely, cooling and insulating. The ability of the oil to successfully provide these functions is greatly dependent on the physical and chemical integrity of the mineral oil which needs to confirm to specific criteria for it to be used effectively within transformers.

- Mineral oil will always undergo oxidation when circulating as a cooling and insulating media in electrical equipment. It is only the degree of oxidation that can and should be reduced where possible. The rate of oxidation is determined by the oil temperature and the concentrations of oxygen and moisture present in both the oil and the equipment.

- The natural inhibitors contained in uninhibited mineral oil are continuously being depleted as they limit the rate at which oxidation occurs while the oil is in-service. Unlike artificially inhibited mineral oils, the natural inhibitors cannot be replenished as the addition of artificial inhibitor would affect the ageing patterns of the oil and ultimately affect the condition monitoring trending patterns for such equipment.

- The process of oxidation produces by-products which in themselves promote further oxidation and ultimately a chain reaction. Oxidation negatively affects many of the oil properties such as oxidation stability, dielectric strength, acidity, moisture content, etc.

- PCBs are synthetic substances with high thermal and chemical stability which made them ideal for use as insulating and cooling media in electrical equipment. It is unfortunately these same characteristics which render PCBs persistent organic pollutants.

- PCBs were first produced in the United States in the late 1920's. PCBs were produced under a various trade names across the globe. Production was ceased in the late 1970's after their toxic and bio-accumulative properties became widely known.

- PCBs settle in the fatty tissue and liver of the human body. The World Health Organisation has rated PCBs as potential carcinogens.

- South Africa is a party to the Stockholm Convention on Persistent Organic Pollutants. The Convention has earmarked the eradication of PCBs from use by 2025 and for lower concentration, no later than 2028.

- Owners of PCB materials have to comply with several national laws and standards which govern and impact the manner in which PCBs are managed and disposed of within South Africa.

- As a hazardous material, PCBs require specialized methods of destruction and disposal. Disposal of PCBs can only be undertaken at facilities licensed by the South African Minister of Water Affairs.

- PCB (in oil) concentrations less than 50ppm are classified as PCB-free under the Stockholm convention. However, as part of good corporate governance and risk mitigation, Eskom and other international electricity utilities are working towards total eradication of PCBs from its insulating oil and equipment. PCB contaminated oil at concentrations just below 50ppm may still result in significant PCB soil contamination should a spill occur. This is due to the fact that the SANS 290 limits for PCBs in soil are significantly more stringent and range from 0.5 ppm for agricultural land to 10ppm for commercial or industrial land.

- The process of PCB dechlorination is well established and several variations of the technology used for PCB dechlorination are commercially available throughout the world. The process effectively destroys PCB molecules through the addition of an alkali or alkaline earth metal carbonate, hydroxide or bicarbonate to the contaminated medium thereby replacing the chlorine atoms on the PCB molecules with hydrogen. The process allows for the recovery of dechlorinated oil for reuse.

- Sodium based dechlorination methods typically use a sodium metal dispersion added to an aromatic radical anion substrate (naphthalide) in the presence of an ether-type solvent (tetrahydrofuran) to produce an alkali metal aromatic radical anion reagent (sodium naphthalenide). The reagent is added to the PCB contaminated oil to bring about a reaction with the chlorine atoms on the PCB molecules. The chlorine atoms are converted to an inorganic salts and the chlorine-free polymeric structures (or biphenyls) fraction is removed by organic fraction filtration or centrifugation.

- The effect of sodium dechlorination on the natural inhibitors of uninhibited mineral oil is not well documented. Two sources of literature reviewed briefly mention the reduction of natural inhibitor content after sodium dechlorination, however these statements are not referenced the literature.

- A study evaluating the reaction kinetics of PCB in an oil substrate with sodium metal dispersion particles established that the dechlorination reaction occurs in three steps;

  Step 1: Chemical reaction between the PCB and the sodium particle at interface.
  Step 2: Diffusion of the PCB through the polymer layer generated by the reaction.
  Step 3: Reaction of PCBs with the sodium dispersion after penetration through the polymer layer.

- The efficiency of the sodium dechlorination process can be improved by the use of smaller sodium metal particles within the dispersion.

- Several established and emerging processes are available for the thermal and non-thermal destruction of PCBs. Proven processes involve incineration and land filling of different streams of PCB waste. These are currently the only two process licensed for use within South Africa. Two local companies are currently in the process of obtaining licenses for PCB dechlorination technologies.

- PCB destruction technologies are characterized internationally by its percentage Destruction Efficiency (for non-thermal processes) and the percentage Destruction and Removal Efficiency for thermal processes.

- A common problem with neural networks is that if the network receives an input which is outside the range of the training data, the network response might be far from accurate depending on the complexity of the process that was modelled. This is the problem of extrapolation. Neural networks do not extrapolate well i.e. they can only really predict accurately or interpolate within the range of the training data.

2.14 COMPARATIVE ANALYSIS OF THE BENEFITS OF DECHLORINATION VERSUS LOCAL PCB LICENSED DISPOSAL OPTIONS

Although disposing of Eskom’s PCB contaminated oil at the licensed thermal facility is legal, several factors currently render this option economically and environmentally less viable. This section examines and quantifies, where possible, the financial implications of dechlorination relative to the two PCB disposal options currently licensed within South Africa. It also discusses certain environmental impacts associated with each disposal option. Calculations are based on disposal of 1000 tons of PCB contaminated oil.

2.14.1 ENCAPSULATION & LANDFILLING

In previous years Eskom encapsulated and landfilled its PCB materials. Eskom has subsequently refrained from encapsulating and landfilling of PCB contaminated oil and equipment and currently only landfills PCB contaminated soil. The decision to stop encapsulating PCB oil and equipment was based on the fact that landfilling did not offer complete destruction of the PCB material. Landfilling is for this reason considered more for long term storage without the option of retrieval for reuse.

In accordance with the National Environmental Management Act (1998), Eskom remains liable for any future environmental damages, such as leaching and subsequent ground water contamination, that may occur as a result of an inadequately maintained landfill site. The author did therefore not quantify any financial benefit for this disposal option.

2.14.2 THERMAL TREATMENT

The licensed thermal treatment facility in Gauteng is based on the process of thermal desorption via refractory bricks followed by thermal oxidation. The process, described in subsection 2.10.12, is fully electrically driven and runs 24 hours a day, requiring an average 0.1150 MW of electricity per hour, at 96 % load capacity, and has a PCB feed rate of between 200 kg and 2000 kg of PCB contaminated oil per hour as described in the scoping report for the thermal treatment plant undertaken by Hindoc MSA (2001). The scoping report was produced as part of the environmental impact assessment in fulfilment of the requirements for obtaining a trial license for the operation of a thermal hazardous waste treatment plant during demonstration phase. The feed rate varies depending on the concentration of PCB present in the oil. An average feed rate of 1000 kg per hour of PCB contaminated oil will be used in the calculations pertaining to this technology. Table 1-1 provides information on the amount of coal and water required as well as the amount of carbon dioxide gas produced during generation of 1 kWh of electricity.

The direct estimated cost of thermal disposal of 1000 tons of PCB contaminated oil as charged by the disposal facility is calculated as:

Tonnage X Cost per ton = Cost for disposal
1000 X R 16 000.00 = R 16 000 000.00……………………(11)

The estimated amount of electricity required for thermal disposal of 1000 tons of PCB contaminated oil, based on an average feed rate of 200 kg per hour, is calculated as:

$$\frac{\textit{Tonnage}}{\textit{Feed rate / hour}} = \textit{Total hours}$$

$$\frac{1000 \text{ tons}}{0.2 \text{ tons/hour}} = 5000 \text{ hours} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Total hours X Power Requirement of Plant = Total kWh required

5000 hours x 1150 kW (plant) = 5.75 x 10^6 kWh or 5.75 GWh……………………………..(13)

Table 2-8: Selected resource input required and CO_2 emitted to produce 5.75 GWh of electricity*

Measure	**Unit of Measurement**	**Amount/ KWh ***	**Total needed for Production of 5.75 GWh**
Coal Usage	kg/kWh	0.5	2875 tons
Water Usage	L/kWh	1.35	7762.5 kilo litres
Carbon Dioxide Production	kg/kWh	0.9	5175 tons

*(Eskom Annual Report, 2009: Department of Environmental Affairs- State of the Environment, n.d)

The thermal disposal facility obtains its electricity supply directly from Eskom on the Megaflex rate at a current revenue tariff of 22,5c/kWh. The average production cost per tariff of the Megaflex option is 20,6c/kWh as published in the 2009 Eskom Annual Report (2009).

The production cost of 5.75 GWh at the current rate is calculated as:

20,6c/kWh X 5.75 x10^6 kWh = R 1 184 500.00…………...……...(14)

Revenue recovered from the sale of 5.75 GWh at the current Megaflex tariff rate

22,5c/kWh X 5.75 x10^6 kWh = R 1 293 750.00.…………...……..(15)

Profit derived from sale of electricity = (13) – (12) = R 109 250.00 or 9.2 %........................(16)

Newcomer (2008) cited an environmental emissions tax cost of USD 35 per metric ton of CO_2 produced. An exchange rate of R7.6 per $1, as per economic indicators as at 6th of November 2009 is used.

The carbon dioxide emissions tax associated with the production of 5175 tons of CO_2 for the thermal treatment of PCB oil is calculated as:

Tonnage of carbon dioxide X Cost per metric ton = Carbon emissions tax associated with thermal destruction

5175 tons X R 266.00 = R 1 376 550.00………………………….....(17)

The actual cost incurred by Eskom for thermal destruction of 1000 tons of PCB contaminated oil, excluding costs associated with environmental impacts listed in table 1-1 above, is calculated as:

Actual cost of thermal destruction to Eskom:
Actual cost = (11) + (17) – (16) = R 17 267 300.00…………………………..…………(18)

2.12.4. SODIUM BASED CATALYZED DECHLORINATION

Base catalysed dechlorination processes operate on the principles of chemical reaction of the PCB molecule with an alkali metal or alkali metal oxide or hydroxide. The process is by default considered more environmentally sound as it does not involve combustion and therefore does not have the risk of the production and release of harmful emissions into the atmosphere. Other benefits include that the process allows for the recovery of reusable oil, that the process is mobile and dechlorination can either be undertaken by bulk or continuous processing. The process is also significantly less energy intensive, with the average electricity requirement 150 kWh and a feed rate of up to 3800 litres per hour. The locally available (unlicensed) dechlorination plants are batch type and can treat batch volumes of between 500 to 3800 litres at a time, depending on PCB oil contamination level. It is important to note that the higher the PCB concentration of the contaminated oil, the more reagent and longer reaction time is required to achieve the desired PCB concentration level of below 2ppm. The average time taken for reaction and regeneration of the PCB contaminated oils in the range of 12 to 144 ppm, is 3 hours. Longer reaction times are observed for the PCB concentration above 500 ppm. For this study, processing of the 1730 ppm PCB oil took as long as 8 hours to reduce PCB concentrations of less than 2 ppm, with a total time of 12 hours including oil regeneration after dechlorination.

For simplicity, the author shall assume a conservative dechlorination rate of 287 litres per hour (average batch volume size divided by the average dechlorination and regeneration time). The cost of dechlorination is directly proportional to the PCB concentration of the oil and typically ranges between R8.00 to R 12.00 per litre. The density of used mineral insulating oil is around

0.895 kg/L (Dalton 2008: Nynas 2001). A thousand tons of PCB contaminated oil would be equivalent to 1117[1] kilo litres (kL) of used mineral oil.

The cost of dechlorinating 1000 tons of PCB contaminated mineral oil, assuming an average dechlorination cost of R10 per litre, is calculated as follows:

Volume **X** ***Cost per Litre*** **=** ***Cost of Dechlorination***

1117×10^3 L X R 10.00/L = R 11,170,000.00…………….(19)

The dechlorination cost in calculation (19) will be offset by the cost of the value of the recovered dechlorinated oil, which can either be retained within Eskom or be sold into the used oil market at an estimated average cost of R4.50 per litre. Assuming volume losses of 10% after processing, the value of the recovered commodity is calculated as follows:

Regenerated Oil (l) X Potential Revenue (per litre) = Estimated Potential Revenue

1005.3×10^3 L X R 4.50/L = R 4,523,850.00…………………………...(20)

The estimated amount of electricity required for dechlorination of 1117 kL of PCB contaminated oil (equivalent to 1000 tons), based on an average feed rate of 287 litres per hour, is calculated as:

$$\frac{\textit{Volume}}{\textit{Feed rate / hour}} = \textit{Total hours} \ \ X \ \ \textit{Power Requirement of Plant} = \textit{Total kWh required}$$

$$\frac{1117}{0.287} = 3892 \text{ hours X } 150 \text{ kW (plant)} = 583800 \text{ kWh or } 583.8 \text{ MWh or } 0.58 \text{ GWh} \ldots\ldots\ldots\ldots(21)$$

Table 2-9: Selected resource input required and CO_2 emitted to produce 0.58 GWh of electricity

Measure	**Unit of Measurement**	**Amount/ kWh**	**Total needed for Production of 0.58 GWh**
Coal Usage	kg/kWh	0.5	291.9 tons
Water Usage	L/kWh	1.35	788.1 kL
Carbon Dioxide Production	kg/kWh	0.9	525.4 tons

The carbon dioxide emissions tax associated with the production of 525.4 tons of CO_2 for the dechlorination of 1000 tons of PCB oil is calculated as:

---

[1] The volume of used mineral oil that is equivalent to 1000 tons of mineral oil, without compensating for the density of PCBs contained in the oil which, depending on PCB concentration, is negligible.

Tonnage of carbon dioxide X Cost per metric ton = Carbon emissions tax associated with dechlorination

525.4 tons X R 266.00 per ton = R 139 756.40 ....(22)

As the dechlorination facilities are smaller and do not operate on a 24 hour basis, the author presumes an electricity revenue tariff in line with the Eskom Miniflex tariff option.

The cost associated with generating 0.58 GWh at the current Miniflex rate is calculated as:
24,4c/kWh X 0.58 x10^6 kWh = R 141 520.00……… ………………….……(23)

Revenue recovered from the sale of 0.58 GWh at the current Megaflex tariff rate
26,3c/kWh X 0.58 x10^6 kWh = R 152 540.00…...…………….....(24)

Profit derived from sale of electricity (24) – (23) = R 11 020.00 or 7.8%..............................(25)

The actual cost incurred by Eskom for dechlorination of 1000 tons of PCB contaminated oil, excluding the costs associated with the environmental impacts listed in Table 2-9 above, is calculated as:

Actual cost of dechlorination = [(19) + (22)] – [(20) + (25)] = R 6 774 886.40.…………….(26)

The relative cost benefit associated with the destruction of 1000 tons of PCB oil is calculated as:
(Actual cost of thermal destruction) **-** (Actual cost of dechlorination) = Disposal cost saving

R 17 267 300.00 **-** R 6 774 886.40 = R 10 492 413.60, a cost saving of 61%......................(27)

The cost benefit associated with sodium dechlorination is apparent from calculation (27). The sodium dechlorination method has further significant merit as the use of natural resources is significantly reduced when using this process for PCB destruction.

Chapter Three

EXPERIMENTAL

3.1 INTRODUCTION TO THE EXPERIMENTAL INVESTIGATION

This chapter discusses the experimental methodology employed and the technical operation of the sodium based dechlorination technology. It gives a brief summary of the analytical test methods used to evaluate the selective parameters, relating to oil oxidation stability, of the nine test batches processed during the study.

3.2. EXPERIMENTAL METHODOLOGY

The author collected suitable sample volumes of PCB contaminated oils in the concentrations levels as stipulated by the Stockholm Convention on Persistent Organic Pollutants i.e. below 50 ppm, between 50 and 500 ppm and above 500 ppm. This allowed for the collection of 3 main batches of uninhibited napthenic mineral oil of the Nynas 10GBN type, although it cannot be confirmed if the oil had been mixed or topped up with other uninhibited oil from a different supplier. Volumes of the batches were mixed with each other and similar oils containing lower PCB concentrations in order to obtain a spread of concentrations within each of the three PCB ranges stipulated by the Stockholm Convention. Samples were taken as follows for of the ranges processed:

- Prior to energizing i.e. control sample for baseline data
- After PCB dechlorination, to assess the effects of sodium dechlorination on the oil.
- After oil regeneration, to assess the oil’s suitability for reuse in transformers.

The samples were submitted to accredited analytical laboratories, within and external to Eskom, for the following analyses.

- PCB Analysis
- Oxidation Stability
- PAH Analysis
- Percentage Total Sulphur
- Karl-Fischer Moisture Content
- Acidity Content
- Dielectric Strength

3.3 DESCRIPTION OF PROCESS & EQUIPMENT USED IN EXPERIMENTAL WORK

The sodium dechlorination process consists of two phases. The first phase involves the drying and filtration of the PCB contaminated oil. This is done as a mitigation measure to prevent the violent reaction of sodium with moisture. The second phase comprises the dechlorination / chemical reaction process, which involves the introduction of metallic sodium dispersion, an aromatic radical anion substrate and a hydrogen donor, typically from a solvent such as Tetrahydrofuran (THF).

The sodium reacts with the PCB molecule and effectively breaks the weaker carbon-chlorine bond to form sodium chloride, which is removed from the process. The dechlorinated oil goes through a centrifuge to remove suspended solids and subsequently undergoes a clay regeneration step to restore the electrical and chemical characteristics that would allow for reuse of the oil as insulating media in electrical equipment. Three batches of each of the three PCB ranges described in table 3 below were processed for evaluation.

Table 3-1: Ranges of PCB Contaminated Oil for Processing

PCB Range	PCB Contamination Level
1	<50 parts per million
2	50 – 500 parts per million
3	> 500 parts per million

3.3.1 STEP-BY-STEP SODIUM DECHLORINATION PROCESS

To fully understand the operation of the sodium dechlorination process employed in Chapter 3 of this study, the step-by-step process explained in this subsection must be read in conjunction with the flow diagram contained in Figure 3-1.

- *Step 1:* PCB contaminated oil enters the dechlorinator at the system INLET and passes through HEAT EXCHANGER (1) where it is heated to between 65 and 70^{o}C to remove excess moisture. The heating time is dependant on the moisture concentration of the PCB contaminated oil entering the system. For safety reasons the moisture concentration of the heated oil existing (1) does not exceed 30 ppm, as sodium metal dispersion is used in the dechlorination process.

- *Step 2:* The heated oil then passes through PUMP (1) into the HEATER where the temperature is raised to between 120^{O}C to 130^{O}C. The pipes following the heater are insulated to ensure the oil temperature is maintained.

- *Step 3:* The heated oil is then pumped into the MIXING CHAMBER where it will encounter a predetermined volume of the sodium reagent either only sodium metal dispersion or a mixture of sodium metal dispersion, naphthalene and tetrahydrofuran, which has been pumped into the mixing chamber via the INJECTOR. The heated PCB contaminated oil and sodium reagent are thoroughly mixed.

- *Step 4:* The mixture flows in to the REACTION ZONE where the dechlorination reaction is completed and the sodium is reacted with the chlorine atoms on the PCB molecules contained in the mineral oil. The dechlorination reaction of the PCB molecule is limited to the amount of active sodium present, resulting in the formation of sodium chloride. The reaction path is as follows:

$$\mathbf{XCl} + \mathbf{Na^{R}} \Longrightarrow \mathbf{NaCl} + \mathbf{X^{o}} \qquad \text{………………(28)}$$

  Where:
  XCl is a PCB molecule *(1 to 10 chlorine atoms)*
  Na^{R} is a reactive sodium atom
  X^{o} is a biphenyl molecule *(chlorine free)*

- *Step 5:* It is possible to neutralise and remove the un-reacted reagent and catalyst through the addition of water and carbon dioxide. The resulting hydrogen gas developed in the vessel is vented to atmosphere. A screw pump continuously drains the vessel and feeds the PCB free oil/water mixture into a centrifuge for removal of salts and particles

- *Step 6:* The temperature of the decontaminated oil is reduced to the below the melting point of the sodium to allow the molten sodium to solidify and separate out of the oil.

- *Step 7:* To achieve the drop in temperature the decontaminated oil leaves the reaction zone and flows through HEAT EXCHANGER 2, where it releases heat and flows into HEAT EXCHANGER 1 where further heat release occurs. This heat is subsequently used to heat the PCB contaminated oil entering the system.

- *Step 8:* The cooled dechlorinated oil leaves HEAT EXCHANGER 1 (at below 80^{O}C) and passes into the SEPARATOR (centrifuge) where the solidified sodium is removed from the system. Lowering the oil temperature to below 80^{O}C also allows for the separation of the polymer by-product from the oil through filtration or centrifugation.

- *Step 9:* The dechlorinated oil leaves the SEPARATOR and is pumped back through both HEAT EXCHANGERS to raise the temperature. This is done as higher oil temperatures aid in oil degassing.

- *Step 10:* The decontaminated oil is degassed in the degasser and sent to the holding tank or straight into the regeneration plant.

3.2.2 DECHLORINATED OIL REGENERATION

The dechlorinated oil is fed through a Fullers Earth Clay regeneration process to purify and restore specific chemical and electrical characteristics of the oil as discussed in section 2.11 so as to conform to the requirement regenerated oil as specified in the SANS 555 standard and contained in Table 2-2 (Dalton, 2008).

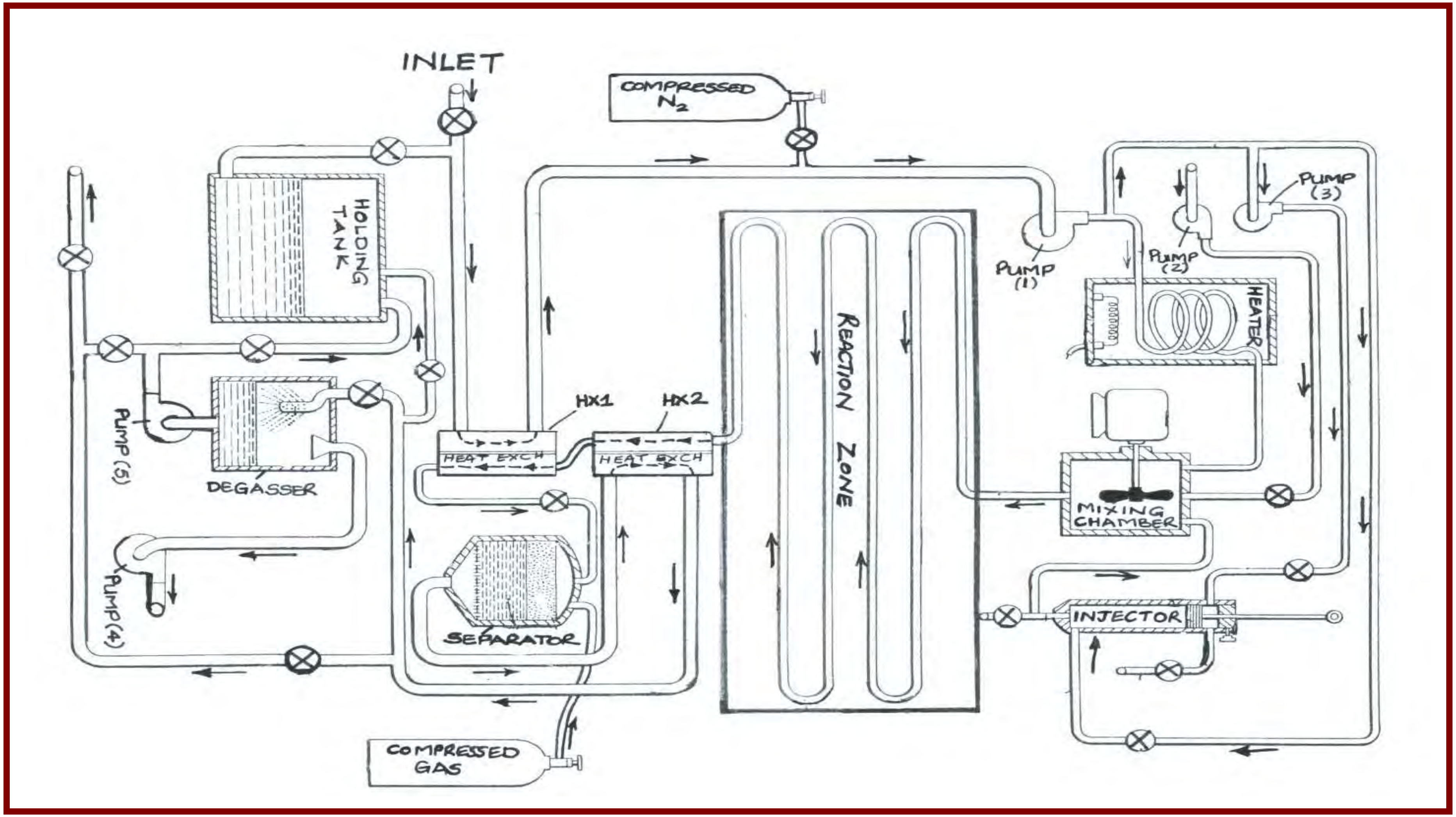


Figure 3-1: Sodium Dechlorination Process Flow (Jordan, 1982)

Figure 3-2: Mobile sodium dechlorination plant

Figure 3-3: Reagent / injector dosing

Figure 3-4: Centrifuge – separation

Figure 3-5: Sample collection

3.4. CHEMICAL ANALYSES OF UNIHBITED DECHLORINATED MINERAL OIL

The oil in a transformer acts as both a cooling and insulating media. One can therefore draw the analogy that the oil in a transformer is much like the blood in the human body in that it contains information on the health of the transformer. Analysis of a transformer oil sample contains a wealth of information that may assist an operator in making crucial decisions on whether or not to remove the transformer from service in order to prevent a potential catastrophe and unplanned outage.

A number of chemical analyses techniques have been developed and proven over the years, and are currently being used as reliable pro-active and preventative monitoring tools within power utilities across the globe. The chemical analyses relevant to this study are briefly explained below.

3.4.1 POLYCHLORINATED BIPHENYL ANALYSIS

As described in section 2.5, 209 variations (congeners) exist. New oil produced from crude oil does not contain PCBs. The congeners most commonly used as insulating and cooling media in electrical equipment are Askarels with unique identifiers namely; 1260, 1254, 1248 and 1242. The "12" contained in the unique identifier indicates the number of carbon atoms in the biphenyl ring whereas the "60", "54", "48" and "42" indicate the percentage chlorination around the biphenyl molecule. This analysis was performed using the IEC 61619 test method for the determination of PCBs using a high resolution capillary column and an electron capture detector.

3.4.2 MOISTURE CONTENT

Moisture, even in minute quantities, is harmful in power transformers and power equipment as moisture has a tendency to migrate towards areas where the most significant electrical stress exist and where it has the greatest detrimental effect. Moisture accelerates the deterioration of both the uninhibited mineral oil and the insulating materials used inside the transformer. Once deterioration has been initiated, more moisture is produced. This is a self-supporting cycle and once the paper has been degraded, it can never be returned to its original condition. Moisture, either on its own, or in conjunction with cellulose particles also has a detrimental effect on the dielectric properties of oil. Where moisture concentrations and cellulose deterioration rates are sufficiently high, free water may be formed as a by-product in the transformer, which can lead to electrical breakdown. Moisture can be readily removed from the oil however, most of the moisture in a transformer is located in the solid insulation of the transformer (i.e. cellulose insulation paper around copper windings and insulation pressboard) the removal of moisture is not effective without first removing the moisture in the solid insulation. Therefore, there is no “quick fix” solution in the case of a transformer with high levels of moisture. Oil can be damaged during this process and it is best to test the oil after regeneration to ensure compliance with the relevant standards. Moisture analysis for this study was performed using accredited test method IEC 60814.

3.4.3 ACIDITY OR NEUTRALISATION VALUE

The neutralization value of the oil is a measure of the presence of acidic compounds in the oil. An increase in the neutralization number typically indicates oxidation of the oil. The concentration of acids is negligible in new or virgin oil, but increases as a result of oxidative ageing. Acidity is normally used as a measure to decide when oil should be replaced or regenerated. Failure to proceed with these actions will cause the oil to become corrosive, produce dissolved sludge and finally sludge deposits. These deposits can result in overheating and the acid will further weaken the solid insulation material, resulting in eventual failure of the transformer. The acids will also increase the solubility of moisture in the oil and paper, due to the polar nature of these compounds. The acidity analysis for this study was performed using accredited test method IEC 62021-1. This analysis was undertaken by the author..

3.4.4 DIELECTRIC STRENGTH

In transformers, oil is used in conjunction with oil-impregnated paper to provide insulation. However, oil is not as good as insulator as the oil-impregnated paper. The dielectric constant of oil is less than that of paper so that the oil tends to be more stressed than the paper. As a result of this, it may be stated that oil is the weak link in the transformer and that the condition of the oil is of great importance. The maintenance of the oil is paramount to maintain the dielectric strength properties of the oil. Dielectric strength is therefore the insulation property that the oil inherently displays. The dielectric strength analysis for this study was performed using accredited test method IEC 60156 and is described in further detail in chapter 4.

3.4.5 OXIDATION STABILITY

Mineral insulating oil is expected to effectively cool and insulate transformers under stressful operating conditions. Oxidation stability is a crucial characteristic of insulating oil as it measures the ability of the oil to withstand degradation by oxidation. During the oxidation, acids and sludge are formed in the oil, which attack materials within the transformer causing the materials to eventually fail. The function of the oxidation stability test is to determine how long the process would take before unacceptable levels of acids and sludge are reached. The longer the oil can withstand the oxidation process the better it will be for the sensitive materials such as the cellulose insulating paper and metal components contained in the transformer. The oxidation stability analysis for this study was performed in accordance with accredited test methods ASTM D2440/IEC61125 Method C, where oil will be exposed to oxygen in the presence of a copper catalyst for a period 164 hours. The percentage sludge formation and neutralisation number was measured to establish the oxidation stability of the uninhibited mineral oil. This analysis was undertaken by the author with the assistance of the laboratory technician.

3.4.5 POLYAROMATIC HYDROCABONS (PAHs)

PAHs relate to the percentage of hydrocarbon cyclic compounds present in the oil. An aromatic hydrocarbon typically has a benzene structure which is fused to other benzene related hydrocarbons. The dechlorination process typically strips the chlorine off the PCB molecule and replaces it with either an H or an OH depending on the reagent being used in the dechlorination process. PAHs are usually kept as low as possible due to the carcinogenic related tendencies and a maximum of 3% is allowed in mineral insulating oils as cited in the Eskom research report on PAHs in transformer oils (Lombard 2000). The PAH analysis for this study was performed using High Performance Liquid Chromatography (HPLC) test method BS 2000 par 346. The author is not proficient in HPLC instrumentation operation and analysis was therefore undertaken by the laboratory chemist responsible for this area.

3.4.6 TOTAL SULPHUR CONTENT (%)

The test measures the total sulphur content of the oil. The test is performed via X-ray method, ISO14596, to measure total sulphur content. The student is not proficient in the operation of X-ray Diffraction instrumentation and analysis was therefore undertaken by the laboratory chemist responsible for this area.

Chapter Four

EVALUATION & INTERPRETATION OF RESULTS

4.1 INTRODUCTION TO EVALUATION & INTERPRETATION OF RESULTS

A total of nine batches of PCB contaminated mineral oil were processed using the sodium dechlorination technology described in chapter 3. The samples were submitted for chemical analyses, the results, of which are interpreted in this chapter.

4.2. RESULTS OBTAINED

Three samples of each of the nine test batches were taken at specific positions during the experimental part of this study. The first sample was taken prior to PCB dechlorination to establish a baseline. The second sample was taken after dechlorination and a third sample was taken after oil regeneration. The second and third samples were taken to establish the effects of each of the processes (i.e. dechlorination and regeneration) on the specific characteristic/parameter within the oil.

PCB analysis was performed on each of the nine test batches. The test method, IEC 61619, was employed for analysis of the samples taken during the experimental part in this study. This test method involves a solvent extraction step where the 0.2g sample oil is added to a 10 mL volumetric flask together with 1 mL sulphuric acid and 1 mL of 1 ppm decachlorobiphenyl as an internal standard. The contents of the volumetric flask are made up to the mark with hexane, shaken and left to stand until it produces a clear solution. A gas-tight glass syringe is used to draw a 1 µL sample from the volumetric flask. This is introduced into a gas chromatograph (GC) with a high resolution capillary separation column an electron capture detector to allow for qualitative analytical analysis. Specific PCB congeners are represented by peaks on a chromatogram which elute from the GC separation column at specified times. The peak size and areas are indicative of the concentration of the specific PCB congener. Table 4-1 contains the results of each of the nine batches analysed using test method IEC 61619.

Table 4-1: Results of PCB analysis for all samples across the PCB range

PCB Range	**Batch No.**	**Pre-dechlorination**	**Post-dechlorination**	**After regeneration**	**No. of Dechlorination cycles**
Range 1 (<50 ppm)	1	12 ppm	<2 ppm	<2 ppm	1
	2	28 ppm	<2 ppm	<2 ppm	1
	3	41 ppm	<2 ppm	<2 ppm	1
Range 2 (50–500 ppm)	4	58 ppm	<2 ppm	<2 ppm	1
	5	133 ppm	<2 ppm	<2 ppm	2
	6	144 ppm	<2 ppm	<2 ppm	2
Range 3 (>500 ppm)	7	631 ppm	<2 ppm	<2 ppm	3
	8	837 ppm	<2 ppm	<2 ppm	3
	9	1730 ppm	<2 ppm	<2 ppm	4

The oxidation stability test was undertaken by the author with the assistance of the laboratory technician. The test involves the exposure of 25grams of sample oil to a continuous flow of oxygen, at a flow rate of 1L/hour and in the presence of a copper catalyst, for a period of 164 hours and at a constant temperature of 100^{o}C. The copper catalyst is added at a ratio of 0.39 sq.cm/g Oil. At the end of the 164 hour test the sample is analysed to establish its acidity and sludge contents. Tables 4-2 and 4-3 below contain the results of the sludge analysis and titrametric acidity analysis respectively.

Table 4-2: Oxidation stability results as % sludge formation for samples in PCB test range

PCB Range	**Batch No.**	**PCB concentration prior to dechlorination**	**Pre-dechlorination**	**Post-dechlorination**	**After regeneration**
			Sludge after 164h @ 120ºC (% by mass)	**Sludge after 164h @ 120ºC** (% by mass)	**Sludge after 164h @ 120ºC** (% by mass)
Range 1 (<50 ppm)	1	12 ppm	0.68	0.42	0.54
	2	28 ppm	0.55	0.71	0.68
	3	41 ppm	TNP[*]	0.99	0.36
Range 2 (50–500 ppm)	4	58 ppm	0.47	1.37	0.26
	5	133 ppm	0.46	1.65	0.78
	6	144 ppm	0.61	1.87	0.63
Range 3 (>500 ppm)	7	631 ppm	0.38	0.92	0.50
	8	837 ppm	0.67	2.06	1.06
	9	1730 ppm	0.74	2.30	1.40

Table 4-3: Oxidation stability results as acidity content for samples in the PCB test range

PCB Range	**Batch No.**	**PCB concentration prior to dechlorination**	**Pre-dechlorination**	**Post-dechlorination**	**After regeneration**
			Acidity after 164h @ 120ºC (mgKOH/g)	**Acidity after 164h @ 120 ºC** (mgKOH/g)	**Acidity after 164h @ 120ºC** (mgKOH/g)
Range 1 (<50 ppm)	1	12 ppm	1.18	1.14	0.72
	2	28 ppm	1.28	1.23	0.65
	3	41 ppm	TNP[*]	1.50	0.31
Range 2 (50–500 ppm)	4	58 ppm	1.02	1.19	0.74
	5	133 ppm	0.95	1.46	1.58
	6	144 ppm	1.12	1.77	1.25
Range 3 (>500 ppm)	7	631 ppm	1.05	1.56	0.88
	8	837 ppm	0.85	2.50	1.13
	9	1730 ppm	1.12	3.02	1.62

The PAH analysis was undertaken by test method BS 2000 par 346 using High Performance Liquid Chromatography. The procedure is designed to determine the presence and quantities of polycyclic aromatics in unused lubricating base oils and asphaltene free petroleum

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[*] Test not performed as sample was accidentally discarded by laboratory staff prior to analysis

fractions using the dimethyl sulphoxide extraction refractive index method. Table 4-4 contains the PAH results of the samples analysed. Due to the cost associated with this test only six of the nine samples were submitted for PAH analysis. The author did not undertake the PAH analysis.

Table 4-4: Results of polyaromatic hydrocarbon analysis for samples in the PCB test range.

PCB Range	**Batch No.**	**PCB concentration prior to dechlorination**	**Pre-dechlorination**	**Post-dechlorination**	**After regeneration**
			PAH (%)	**PAH** (%)	**PAH** (%)
Range 1 (<50 ppm)	1	12 ppm	1.37	1.34	1.21
	2	28 ppm	0.27	0.28	0.24
	3	41 ppm	-	-	-
Range 2 (50–500 ppm)	4	58 ppm	0.22	0.22	0.20
	5	133 ppm	-	-	-
	6	144 ppm	0.35	0.31	0.32
Range 3 (>500 ppm)	7	631 ppm	0.55	0.57	0.78
	8	837 ppm	-	-	-
	9	1730 ppm	0.49	0.56	0.55

Certain sulphur compounds contained in mineral insulating oil act as natural antioxidants. The ISO 14596 test method was specifically designed to measure the percentage of sulphur in petroleum based products with typical total sulphur contents in the range of 0.001 to 2.5%. The test method makes use of wavelength-dispersive X-ray fluorescence (XRF) spectrometry for quantitative determination. The author did not undertake the analysis.

Table 4-5: Results of the total sulphur content analysis for samples in the PCB test range.

PCB Range	**Batch No.**	**PCB concentration prior to dechlorination**	**Pre-dechlorination**	**Post-dechlorination**	**After regeneration**
			Total Sulphur (%)	**Total Sulphur** (%)	**Total Sulphur** (%)
Range 1 (<50 ppm)	1	12 ppm	0.18	0.16	0.14
	2	28 ppm	0.18	0.16	0.13
	3	41 ppm	-	-	-
Range 2 (50–500 ppm)	4	58 ppm	0.17	0.14	0.13
	5	133 ppm	0.20	0.16	0.14
	6	144 ppm	-	-	-
Range 3 (>500 ppm)	7	631 ppm	-	-	-
	8	837 ppm	0.19	0.16	0.12
	9	1730 ppm	0.18	0.13	0.12

The moisture content of the sample batches were determined using test method IEC 60814. The test determines the concentration of moisture in insulating oils using a coulometrically generated Karl Fischer reagent.

The instrument has a titration cell that contains an anode solution (a mixture of an alcohol, a base, sulphur dioxide and iodine) and an analyte. The titration cell contains a Platinum anode which electrically generates iodine and is immersed in the anode mixture. One millilitre (mL) of oil sample is introduced to the titration cell and the iodine reacts with the water contained in the sample. The amount of current used to generate the iodine to reach the end point of the titration, is used to calculate the water concentration in the sample. The author carried out this analysis and the results thereof are contained in Table 4-6.

Table 4-6: Results of the moisture analysis for samples in the PCB test range

PCB Range	**Batch Number**	**Pre-dechlorination**	**Post-dechlorination**	**After regeneration**
Range 1 (<50 ppm)	1	338 ppm	34 ppm	12 ppm
	2	124 ppm	28 ppm	8 ppm
	3	63 ppm	17 ppm	9 ppm
Range 2 (50 – 500 ppm)	4	78 ppm	33 ppm	5 ppm
	5	61 ppm	26 ppm	18 ppm
	6	144 ppm	24 ppm	7 ppm
Range 3 (>500 ppm)	7	631 ppm	25 ppm	8 ppm
	8	837 ppm	29 ppm	3 ppm
	9	1730 ppm	34 ppm	11 ppm

The dielectric strength analysis was undertaken by the author in the Eskom SABS accredited laboratory and was performed in accordance with test method IEC 60156 for the determination of the breakdown voltage at power frequency of the oil sample batches. The test involves the addition of 500 mL of sample oil to a sample cell containing two mounted brass electrodes separated by a gap of 2.5 cm. The dielectric strength (kV) tester applies an increasing voltage across the two electrodes at a rate of 2kV/second until a flash appears between the two electrodes when a specific voltage is reached. This is known as the oil's breakdown voltage or the maximum voltage at which the oil can withstand electrical stresses. The breakdown voltage of oil is reduced by impurities such as dust, floating particles, water content, etc. The results of the dielectric strength tests are contained in Table 4-7.

Table 4-7: Dielectric strength results for samples in the PCB test range

PCB Range	**Batch Number**	**Pre-dechlorination**	**Post-dechlorination**	**After regeneration**
Range 1 (<50 ppm)	1	Not performed	Not performed	Not performed
	2	47 kV	35 kV	69 kV
	3	64 kV	42 kV	78 kV
Range 2 (50 – 500 ppm)	4	51 kV	48 kV	72 kV
	5	59 kV	39 kV	70 kV
	6	43 kV	29 kV	68 kV
Range 3 (>500 ppm)	7	47 kV	43 kV	72 kV
	8	53 kV	38 kV	71 kV
	9	55 kV	39 kV	65 kV

The acidity content or neutralisation value of mineral insulating oil measures the degree to which the oil has oxidized and formed constituents that have acidic characteristics. These constituents include organic acids, phenols, organometallic salts, etc. The test consists of a neutralisation titration where the acid contained in the oil is titrated against a potassium hydroxide base using and a colour indicator to determine the titration end point. This analysis was undertaken by the author in the Eskom SANS accredited laboratory. The results of the neutralisation value test undertaken are contained in Table 4-8.

Table 4-8: Results of neutralisation value analysis for samples in the PCB test range

PCB Range	**Batch Number**	**Pre-dechlorination**	**Post-dechlorination**	**After regeneration**
Range 1 (<50 ppm)	1	0.01 mg KOH/g	0.02 mg KOH/g	0.01 mg KOH/g
	2	0.01 mg KOH/g	0.03 mg KOH/g	0.01 mg KOH/g
	3	0.01 mg KOH/g	0.05 mg KOH/g	0.02 mg KOH/g
Range 2 (50 – 500 ppm)	4	0.05 mg KOH/g	0.06 mg KOH/g	0.02 mg KOH/g
	5	0.03 mg KOH/g	0.01 mg KOH/g	0.03 mg KOH/g
	6	0.03 mg KOH/g	0.04 mg KOH/g	0.01 mg KOH/g
Range 3 (>500 ppm)	7	0.03 mg KOH/g	0.03 mg KOH/g	0.01 mg KOH/g
	8	0.03 mg KOH/g	0.04 mg KOH/g	0.03 mg KOH/g
	9	0.06 mg KOH/g	0.05 mg KOH/g	0.03 mg KOH/g

4.3. EVALUATION & INTERPRETATION OF RESULTS

The PCB results contained in Table 4-1 indicate the efficacy of the sodium dechlorination technology in successfully dechlorinating the PCB content of the contaminated oils. The batches in the <50ppm PCB range required only one cycle of processing to effectively reduce the PCB concentration of the input oil to below 2 ppm PCB. The number of cycles required to achieve the target concentration of <2ppm PCB increases with an increase in PCB input concentration.

Of particular interest are the oxidation stability results and how it relates to the natural inhibitor content of the oil during each phase of the experimental process i.e. pre-dechlorination, post-dechlorination and post-regeneration. Tables 4-4 to 4-8 will be discussed relative to the oxidation stability results contained in Tables 4-2 and 4-3 for each of the three PCB concentration ranges.

4.3.1 EVALUATION AND INTERPRETATION OF SAMPLE RESULTS FOR PCB RANGE <50 PPM

The oxidation stability results obtained in tables 4-2 and 4-3 have been plotted for interpretation purposes.

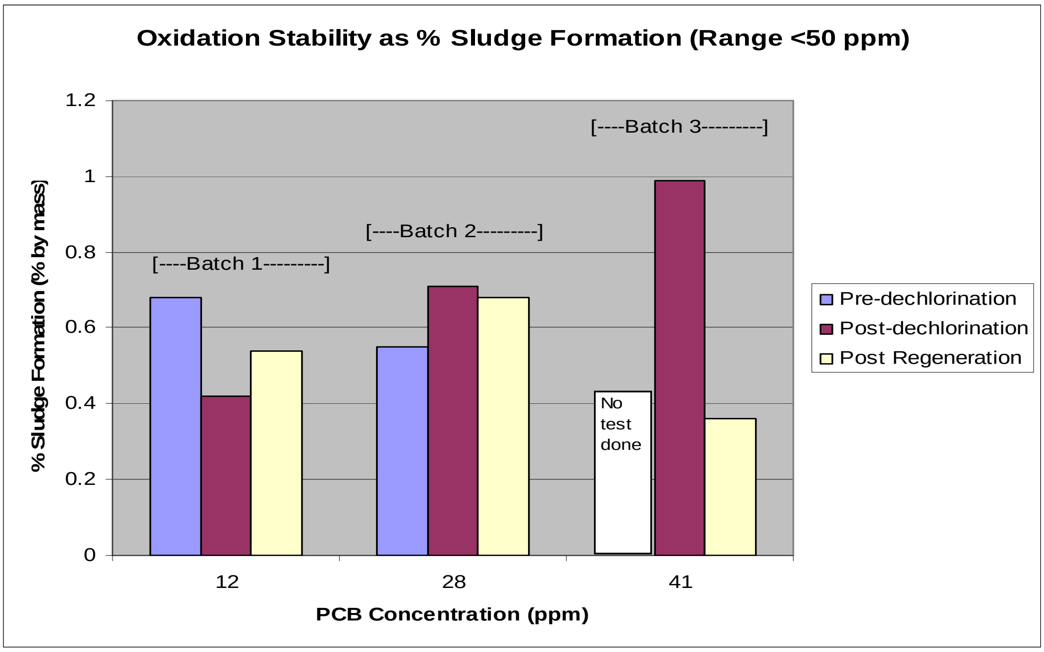

Figure 4-1: Oxidation stability as percentage sludge formation (<50 ppm)

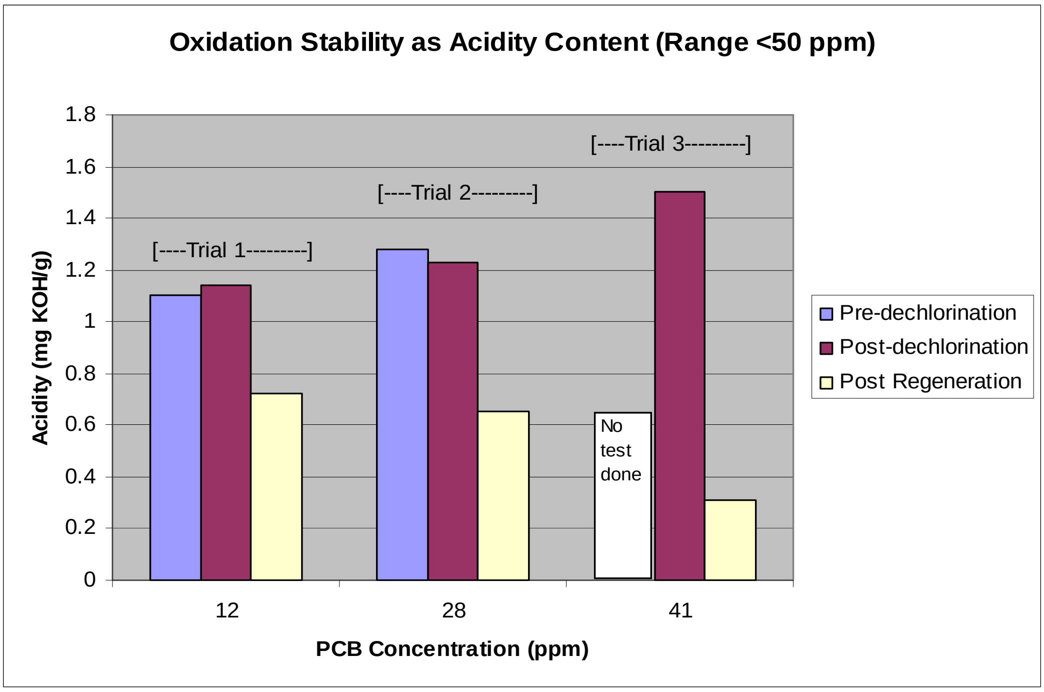

Figure 4-2: Oxidation stability as ppm acidity formation (<50 ppm)

Batch 1 of range <50 ppm indicate lower acid and sludge formation after sodium dechlorination, which indicates an increase oxidation stability after the dechlorination and regeneration process and an overall increase in oxidation stability in the post-regeneration sample. The oxidation stability result ito % sludge formation after regeneration does not appear to conform to the natural behaviour of oil after dechlorination and prior to regeneration as it would be expected that the % sludge formation would be less after oil regeneration. This phenomenon could either be assigned to the influence of external factors such as human error (sample contamination or incorrect measurement). Alternatively it could be due to an inadequate regeneration step due to spent clay thereby not sufficiently removing oxidation enhancing impurities. If so, these impurities may have lead to an accelerated transition of acid to sludge in the post-regeneration sample relative to this transition in the pre-dechlorination sample. Phalavanpour *et al.*(1994) cited that the mechanics of sludge formation in mineral insulating oil occurs in two steps namely:

1. The formation of soluble oxidation products, this process commences as soon as the transformer is energized and the mineral oils starts circulating.
2. The transition of soluble oxidation products such as acids to insoluble tarry like compounds that settle out.

When comparing the post-dechlorination and post-regeneration oxidation stability results it is observed that the acid concentration of the former is higher than that of the later and the % sludge formation of the former is lower than that of the later. This may be due to a faster transition of acid to sludge in the later, if the regeneration process did not adequately remove the oxidation enhancing compounds from the oil.

Batch 2 in the PCB concentration range <50 ppm indicates a distinct increase in percentage sludge formation in the post-dechlorination sample and a decrease in acidity formation. As acid is a precursor for the formation of sludge, it may be inferred that the reaction of acid to sludge occurred more rapidly in batch 2. This could be due to the oil’s solubility of acid being reduced during the dechlorination and regeneration process, however this is not the trend a common trend observed across the ranges and can therefore not be claimed with a large degree of certainty.

It is anticipated that the percentage sludge formation of the pre-dechlorination sample of Batch 3 would have been lower than the post-dechlorination sample although this cannot be confirmed beyond any reasonable doubt as no point of reference i.e. pre-dechlorination sample results, are available to allow for interpretation of the results.

4.3.2 EVALUATION AND INTERPRETATION OF SAMPLE RESULTS FOR PCB RANGE 50 – 500 PPM

Sample/batch 4 of the concentration range 50-500 ppm indicate a decrease in both sludge and acid formation after regeneration indicating oils with higher oxidation stability after the initial pre-dechlorination sample. It could be inferred that the pre-dechlorination samples contained high concentrations of oxidation enhancing compounds such as an acid, moisture and suspended solids. This inference is supported by analytical results for sample 4 reflected in Tables 4-6, 4-7 and 4-8. The presence of a high acid and moisture content in the pre-dechlorination sample would expedite the process of oxidation within the transformer. The high acidity content was removed by clay regeneration process thereby resulting in the lower acid and sludge formation and thereby the higher oxidation stability of the post-regeneration samples for batch 4.

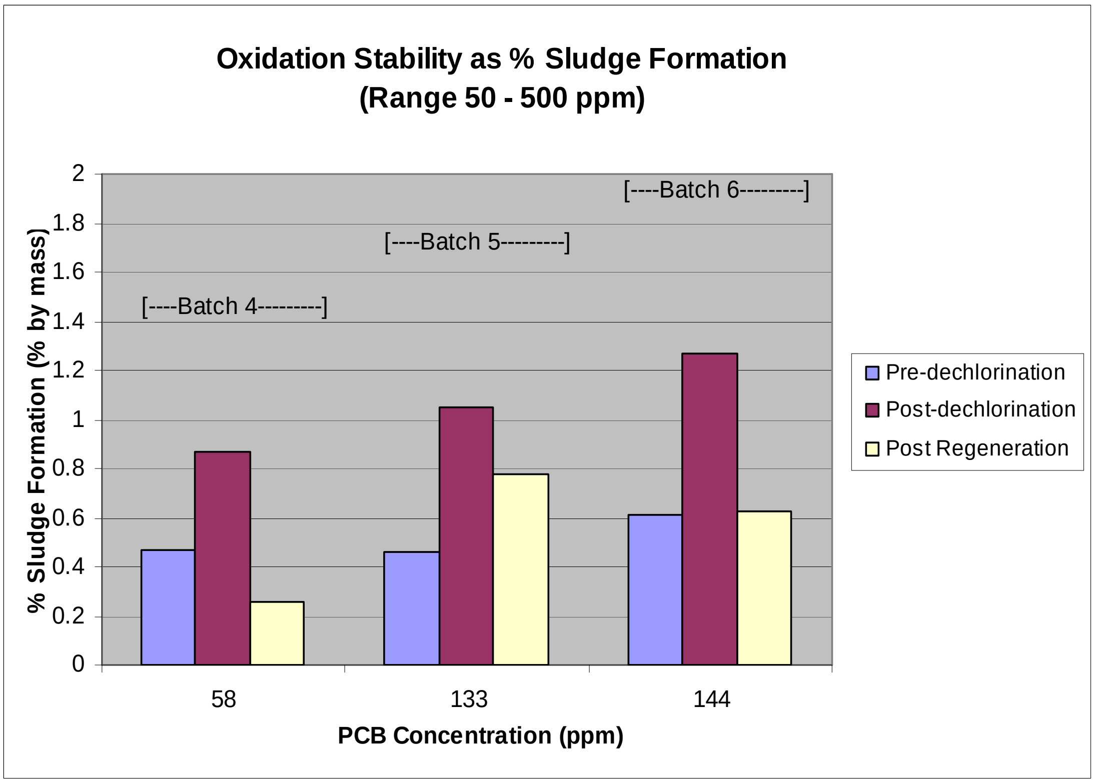

Figure 4-3: Oxidation stability as percentage sludge formation (50 – 500 ppm)

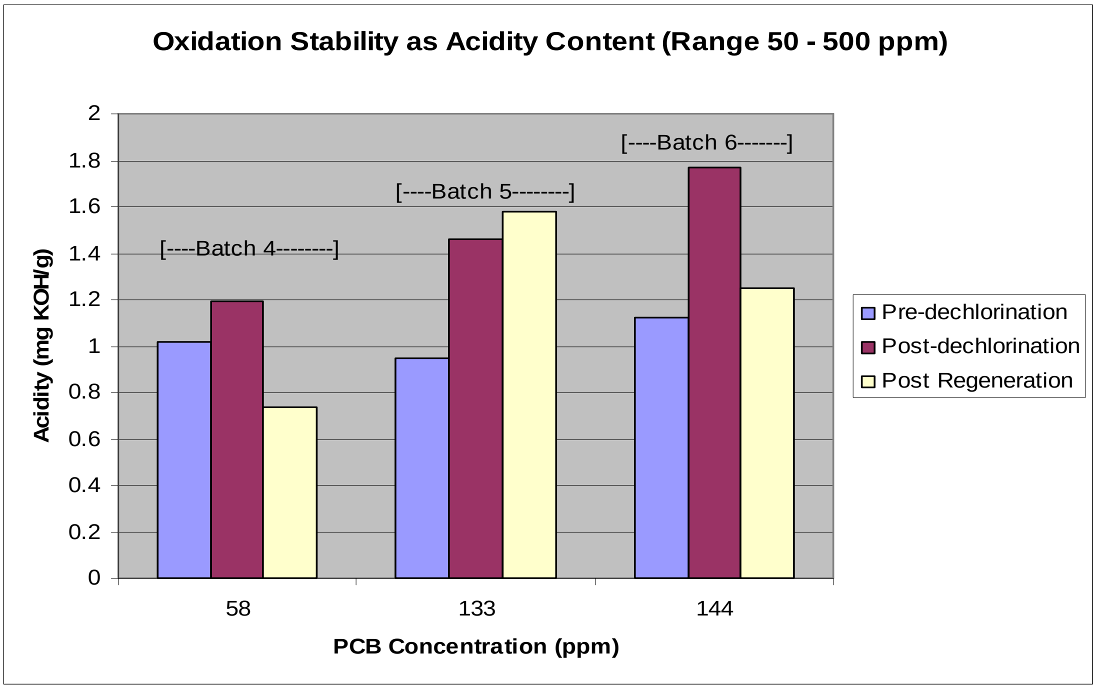

Figure 4-4: Oxidation stability as ppm acidity formation (50 – 500 ppm)

Samples / batch 5 and 6 of PCB concentration range 50 – 500 ppm indicate an increase in both the sludge and acidity of the post-dechlorination and post-regeneration samples relative to the pre-dechlorination sample. Thereby indicating a lower oxidation stability and thereby a lowered natural inhibitor content of the oil after dechlorination and regeneration relative to pre-dechlorination. This could be assigned to the fact that both samples 5 & 6 underwent two dechlorination cycles, resulting in addition of extra dechlorination reagent and longer reaction or contact time and heat exposure. It is hypothesized that the additional dechlorination cycle would have an increased negative impact on the natural inhibitor content of the oil. The results of samples 5 & 6 therefore support the study hypothesis.

4.3.3 EVALUATION AND INTERPRETATION OF SAMPLE RESULTS FOR PCB RANGE >500 PPM

Batches 8 & 9 in the PCB range above 500 ppm indicate an increase in the post-dechlorination and post-regeneration sludge and acidity content. The acidity content of batch 7 increases after dechlorination and decreases to below the pre-dechlorination result obtained for the batch. This could be an error in end-point determination as the acidity analysis is based on a neutralization titration with visual end-point detection. Rendering this test method subjective, to a degree.

From the majority of the results obtained in the PCB range >500 ppm it can be inferred that the natural inhibitor content of the oil is reduced through dechlorination. The regeneration process generally removes the by-products of oxidation, from previous in-service oil ageing processes, to restore most of the oil's chemical and physical properties.

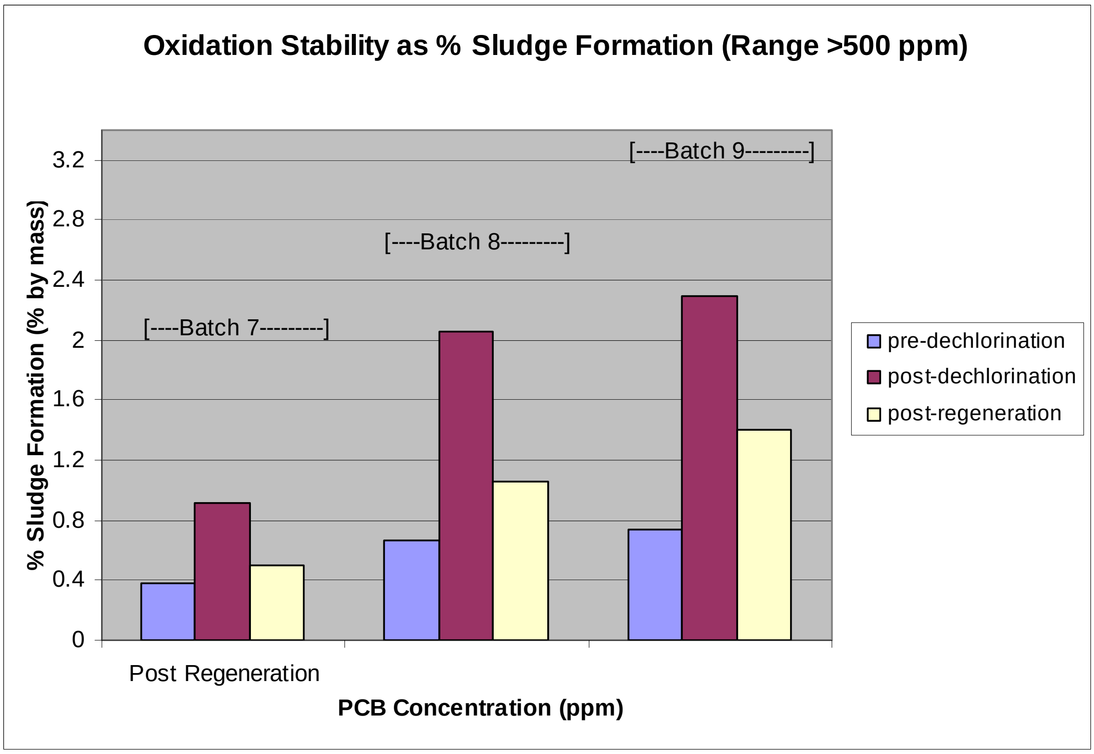

Figure 4-5: Oxidation stability as percentage sludge formation (>500 ppm)

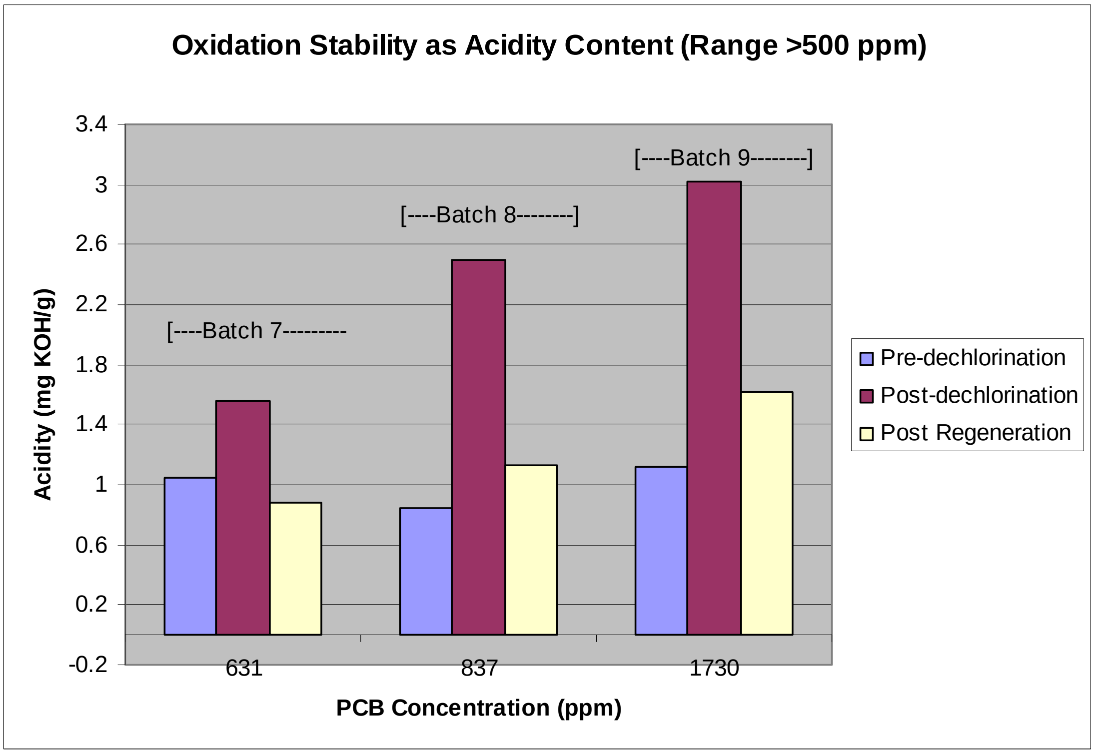

Figure 4-6: Oxidation stability as ppm of acidity formation (>500ppm)

4.3.4 PAH AND TOTAL SULPHUR PERCENTAGE RESULTS

The percentage total sulphur results in table 4-5 indicate a general reduction in sulphur content after dechlorination and regeneration processes. The dechlorination process was found to remove corrosive sulphur from the oil (Lewand, 2008). However, stable sulphur as those found in sulphur based natural inhibitors can become reactive and ultimately corrosive with time and through exposure to high temperatures (Lewand, 2002). Therefore it can be inferred that the older more oxidized an oil is the more likely it is that its stable sulphur (natural inhibitor) will become unstable and corrosive. This process would be further compounded if such oils undergo dechlorination, if the study hypothesis is to be confirmed. The total sulphur content of all the samples analysed indicate reductions after the dechlorination and regeneration processes. However, Phalavanpour *et al* (1994) established that the Fullers' earth regeneration process does not remove the natural inhibitor in the oil. The further reduction in percentage total sulphur after regeneration does therefore not correlate with the findings cited by Phalavanpour et al. (1994). The results of the six samples analysed indicate an average further reduction of 13.8% in total sulphur content after regeneration, which is beyond the 10% deviation or measurement tolerance. The author recommends that this be investigated in further detail outside this study.

The PAH analyses were undertaken to establish whether an increase of this oil parameter would be observed after dechlorination. Although very slight increases in PAH concentration were observed in some cases, not much can be inferred from the results as these increases could be a result of analytical instrument sensitivity. All the samples within the sample range conformed to the SANS 555 specification of less than 3% PAH content.

4.4. TREND EVALUATION OF RESULTS ACROSS THE PCB TEST RANGE

The variations in the effects discussed in subsections 4.3.1, 4.3.2 and 4.3.3 are partly due to natural variability. Figure 4-7 indicates no significant variations in the initial acidity and sludge formation of the pre-dechlorination samples.

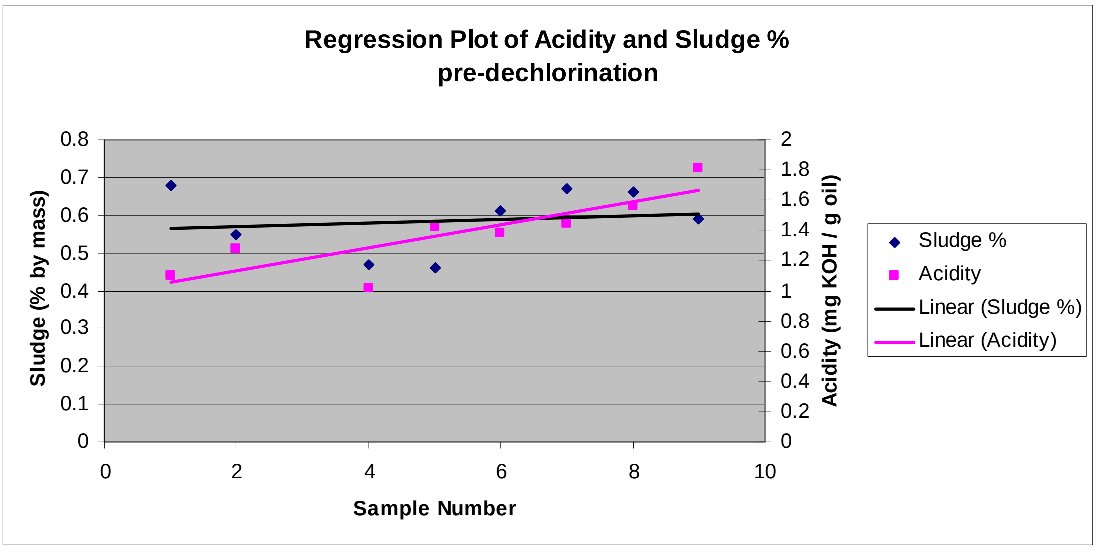

Figure 4-7: Regression plot of acidity and percentage sludge formation prior to dechlorination

The dechlorination process increased the acidity and % sludge formation across all the sample batches, expect sample no.3[2], relative to the results obtained for pre-dechlorination. This infers an overall decrease in the natural inhibitor content after dechlorination.

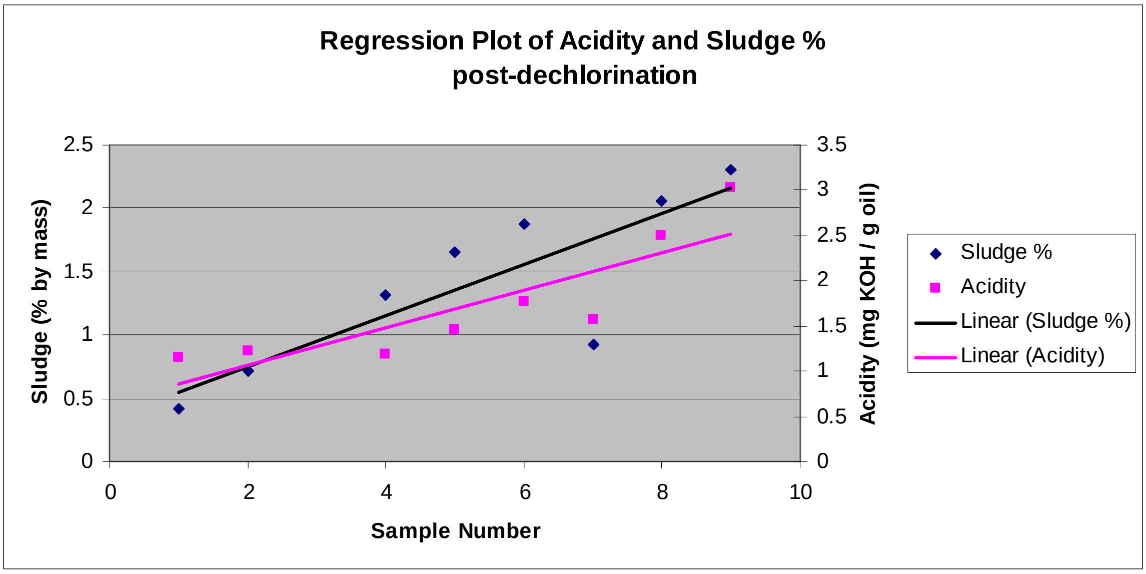

Figure 4-8: Regressions plot of acidity and percentage sludge formation after dechlorination

The percentage variation between the pre- and post-dechlorination results for both acidity and % sludge formation for all samples, except sample no.3, are plotted in Figure 4-9. The average

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[2] Sample no.3 was removed from the data set as no pre-dechlorination results were available.

increase in percentage variation for acidity content and % sludge formation after dechlorination is 15.4% and 41.7% respectively.

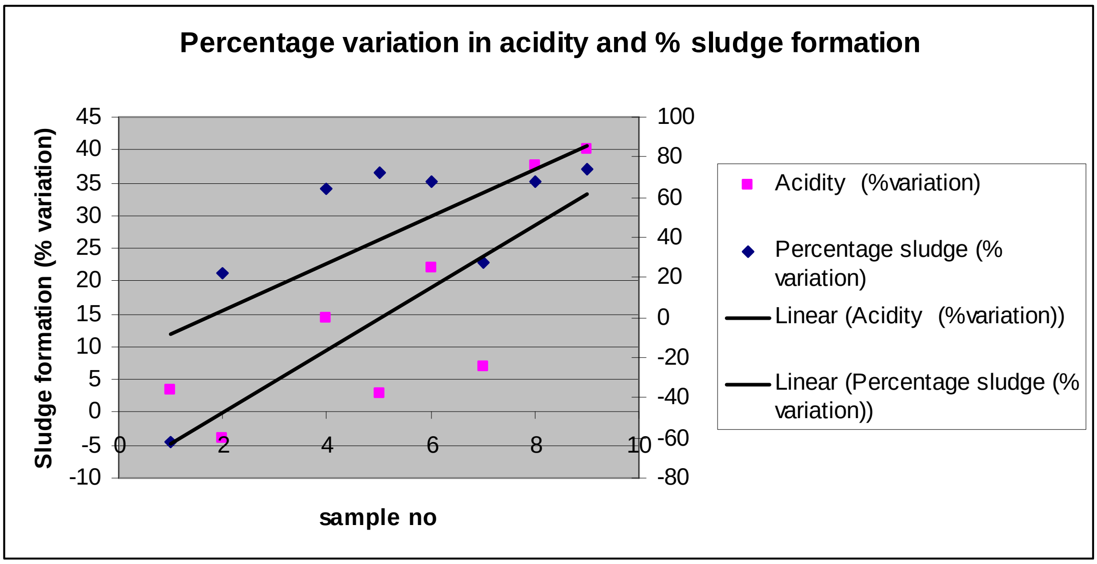

Figure 4-9: Percentage variation in acidity and percentage sludge formation

If a linear trend line is applied to the data set then the pre-and post-dechlorination results for the sample range indicate a higher rate of increase for the percentage variation in % sludge formation compared to that of the percentage variation for acidity content, with increasing PCB concentration.

After regeneration the rate of acid and sludge formation of the oils across the sample range is improved. This is an expected trend as the regeneration process removes acids, polar compounds, suspended solids and other impurities except that of the natural inhibitor, as cited by Pahlavanpour *et al*.(1994), which under normal conditions would accelerate oil oxidation.

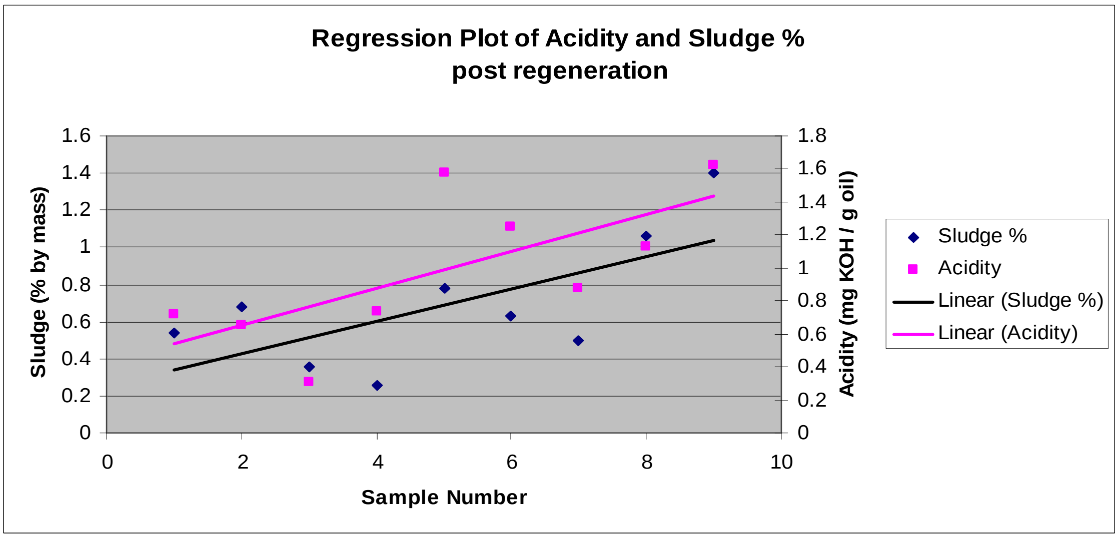

Figure 4-10: Regression plot of acidity and percentage sludge formation after regeneration

A review of the post-regeneration results of the various chemical analyses across the nine sample ranges indicate that most of the samples conform to the specifications as listed in Table 2-2, allowing for re-use of the regenerated oil in electrical equipment provided all other parameters in Table 2-2 are within the specified limits.

Samples 5, 6, 8 and 9 do not conform to the specification for oxidation stability, where samples 8 and 9 are in excess of the limit set for % sludge formation and samples 5, 6 and 9 are in excess of the limit set for acidity content. The percentage PAH concentration of sample 9 is in excess of the 3% limit and is therefore unsuitable for reuse in electrical equipment as cited in the Eskom research report (Lombard, 1996).

Chapter Five

ALGORITHM APPLICATION

5.1 INTRODUCTION TO ALOGRITHM APPLICATION AND THE APPLICATION OF NEURAL NETWORKS TO THIS STUDY

The actual / physical process of sodium based dechlorination, described in chapter 3, and the 164 hour oxidation test, as per American Standards Test Method (ASTM) D 21440, is modelled in this chapter. In simpler terms, oil with known PCB concentrations were process through a sodium dechlorinator. The recovered dechlorinated oil was then exposed to the oxidation stability test which involved continuous exposure of the oil to oxygen and copper for a period of 164 hrs at $120^{0}C$ as seen in Figure 5-1. This resulted in actual input/output data that could be used in the modelling.

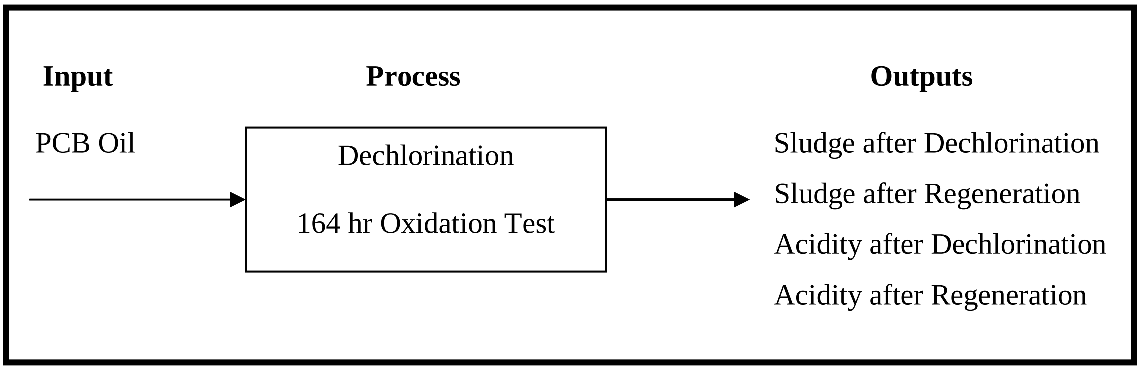

Figure 5-1: Dechlorination and 164 hr Oxidation Test

A sample of the data obtained during the experimental study was used as input and output to establish the algorithm.

The preliminary model established could be utilised as a means of establishing / predicting the effect of the sodium dechlorination process on the oxidation stability (as percentage sludge and ppm acid formation) of the oil without physically having to process the oil through the sodium dechlorinator and subsequently undertaking the 164 hour oxidation stability test.

The training data is seen in Tables 5-1 and 5-2.

Table 5-1: Sample of percentage sludge formation Input and output data (Training Data)

Input	**Outputs**	
PCB-Concentration Prior to Dechlorination (ppm)	Post-Dechlorination Sludge (% by mass)	After Regeneration Sludge (% by mass)
12	0.42	0.54
28	0.71	0.68
58	1.31	0.26
133	1.65	0.78
144	1.87	0.63
631	0.92	0.5
837	2.06	1.06
1730	2.3	1.4

Table 5-2: Sample of acidity concentration input and output data (Training Data)

Input	**Outputs**	
PCB Concentration Prior to Dechlorination (ppm)	Post-Dechlorination Acidity (mg KOH/g)	After Regeneration Acidity (mg KOH/g)
12	1.14	0.72
28	1.23	0.65
58	1.19	0.74
133	1.46	1.58
144	1.77	1.25
631	1.56	0.88
837	2.5	1.13
1730	3.02	1.62

A single neural network was developed using the training data in Tables 5-1 and 5-2. It was developed using a software application called Matrix Laboratory (Matlab) together with an open source neural network toolbox called Netlab. The Matlab / Netlab source code is seen in Appendix 3.

The neural network trained to model the dechlorination and the 164 hour oxidation test has the following parameters:

<u>The network has 1 input as follows:</u>

- PCB Concentration Prior to Dechlorination (ppm).

<u>The network has 4 outputs as follows:</u>

- Post-Dechlorination Sludge (% by mass)
- After Regeneration Sludge (% by mass)
- Post-Dechlorination Acidity (mg KOH/g Oil)
- After Regeneration Acidity (mg KOH/g Oil).

Number of nodes in the hidden layer: 7
Learning rate: 0.04
Number of training cycles: 300

The neural network was then trained. The actual execution of the Matlab / Netlab code is seen in Appendix 4.

5.2 THE RESULTS OBTAINED FROM THE ESTABLISHED ALGORITHM

The results are presented in Tables 5-3 and 5-4. Columns A, B and E were used for training the network. Once the networks weights and biases were found then the data from column A was applied to the network to produce the predicted values seen in columns C and F. The error seen in the table is calculated by first subtracting the values in column C from column B the taking the absolute value of the result. The mean error is calculated by summing all the values in column D and dividing by the number of values i.e. 8.

Appendix 4 also contains each training cycle with the corresponding error. It can clearly be seen that the error decreases after each cycle. Also, the values of the weights and biases can be seen.

Table 5-3: Model 1 - Oxidation Stability as percentage Sludge Formation

A	B	C	D	E	F	G
PCB Conc Prior to Dechlorination (ppm)	Post-Dechlorination Sludge (% by mass)	Model Prediction Sludge (% by mass)	Error = abs(B-C)	After Regeneration Sludge (% by mass)	Model Prediction Sludge (% by mass)	Error = abs(E-F)
12	0.42	0.409474356	0.010525644	0.54	0.553977245	0.013977245
28	0.71	0.726894987	0.016894987	0.68	0.640781689	0.039218311
58	1.31	1.301561125	0.008438875	0.26	0.308562488	0.048562488
133	1.65	1.75639938	0.10639938	0.78	0.679951946	0.100048054
144	1.87	1.750825551	0.119174449	0.63	0.700828931	0.070828931
631	0.92	0.999237454	0.079237454	0.5	0.508388882	0.008388882
837	2.06	1.925200556	0.134799444	1.06	1.090342655	0.030342655
1730	2.3	2.365877746	0.065877746	1.4	1.365723209	0.034276791
	Mean Error =	**ΣD ÷ 8 =**	0.067668498		**Mean Error**	0.043205419

Table 5-4: Model 2 - Oxidation Stability as Percentage Acidity Content

PCB Conc Prior to Dechlorination (ppm)	Post-Dechlorination Acidity (mgKOH/g)	Model Prediction Acidity	Error = abs(B-C)	After Regeneration Acidity (mgKOH/g)	Model Prediction Acidity	Error = abs(E-F)
12	1.14	1.149813928	0.009813928	0.72	0.656110793	0.063889207
28	1.23	1.17099305	0.05900695	0.65	0.680084724	0.030084724
58	1.19	1.242088617	0.052088617	0.74	0.802027558	0.062027558
133	1.46	1.601969252	0.141969252	1.58	1.38803475	0.19196525
144	1.77	1.609728511	0.160271489	1.25	1.408202822	0.158202822
631	1.56	1.648541959	0.088541959	0.88	0.852796589	0.027203411
837	2.5	2.3842175	0.1157825	1.13	1.216687915	0.086687915
1730	3.02	3.058326559	0.038326559	1.62	1.563173961	0.056826039
	Mean Error =	**ΣD ÷ 8 =**	0.083225157		**Mean Error**	0.084610866

Chapter Six

CONCLUSIONS & RECOMMENDATIONS

Nine batches of PCB contaminated mineral oil; three within each of the ranges identified in Table 3-1 were processed using a sodium dechlorination technology. Each batch consisted of 3 samples representing a prior to dechlorination sample, after dechlorination sample and an after regeneration sample.

Based on the results obtained from the experimental tests performed during this study, it can be concluded that the sodium dechlorination process negatively affects the natural inhibitor content of the uninhibited naphthenic based mineral oil.

The degree of reduction in natural inhibitor content appears to be negligible at PCB concentrations below 200 ppm. Post-regeneration samples 5 and 6 did not meet the requirements for oxidation stability test ito acidity content. Post-regeneration samples 1,2,3,4 and 7 conformed to the SANS 555 specification for the parameters measured, allowing for reuse of this oil within transformers[3]. The study did not included samples with PCB concentrations between 200 – 600 ppm, however the establish algorithm can be used to predict the effect of dechlorination on PCB concentrations falling within this region.

The natural inhibitor was greatly reduced in the PCB concentration range >500ppm. This could be assigned to the fact that the contaminated oil in this range endured 3 to 4 cycles of dechlorination prior to reaching the desired PCB concentration of below 2 ppm. Samples from batches 8 & 9 did not conform to the SANS 555 specification for after dechlorination and subsequent regeneration.

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[3] Provided the oils conform to the specifications for all the other parameters set out in SANS555 but not measured during this study.

Most of the Eskom uninhibited PCB contaminated mineral oils currently contained in equipment have been in use for a number of year and their natural inhibitors will have already been reduced. Based on the findings of this study it can be concluded, that for uninhibited PCB contaminated oil above 100 ppm, the natural inhibitor of the oil may not be at a level that would allow for its reuse in transformers. The degree of uncertainty of this conclusion is significantly decreased for uninhibited PCB contaminated oil in the >500 ppm range.

The results obtained from the oxidation stability analyses confirms the author's hypothesis that the dechlorination process removes natural inhibitors such as stable and very stable sulphur (thiophenes) from the oil thus the reduction in oxidation stability observed in the after dechlorination samples of across most of the batches. Possible explanations for this occurrence could be the molecular changes brought about by the introduction of an alkali or alkali earth metal to replace the chlorine atom on the PCB molecule. This causes breaking of the stronger carbon-chlorine bond and at the constant high temperature and pressure at which the dechlorination unit operates, it is hypothesized that some carbon-sulphur bonds may also be compromised during the process, thereby exposing what used to be very stable sulphur and either removing them or rendering them reactive or corrosive.

In order for the neural network to more accurately model the specified process, it is recommended that more training data be used. Again this is data from the actual process. Commercial off the shelf neural software will also provide better results than the open source Netlab that was used. Also, the data that was used to train the neural network was also used to test it. Using another data set to test the network will provide insight into the true capabilities of the network. The author therefore recommends that the preliminary algorithm established during this study be optimised through additional experimental studies, prior to implementation thereof within Eskom.

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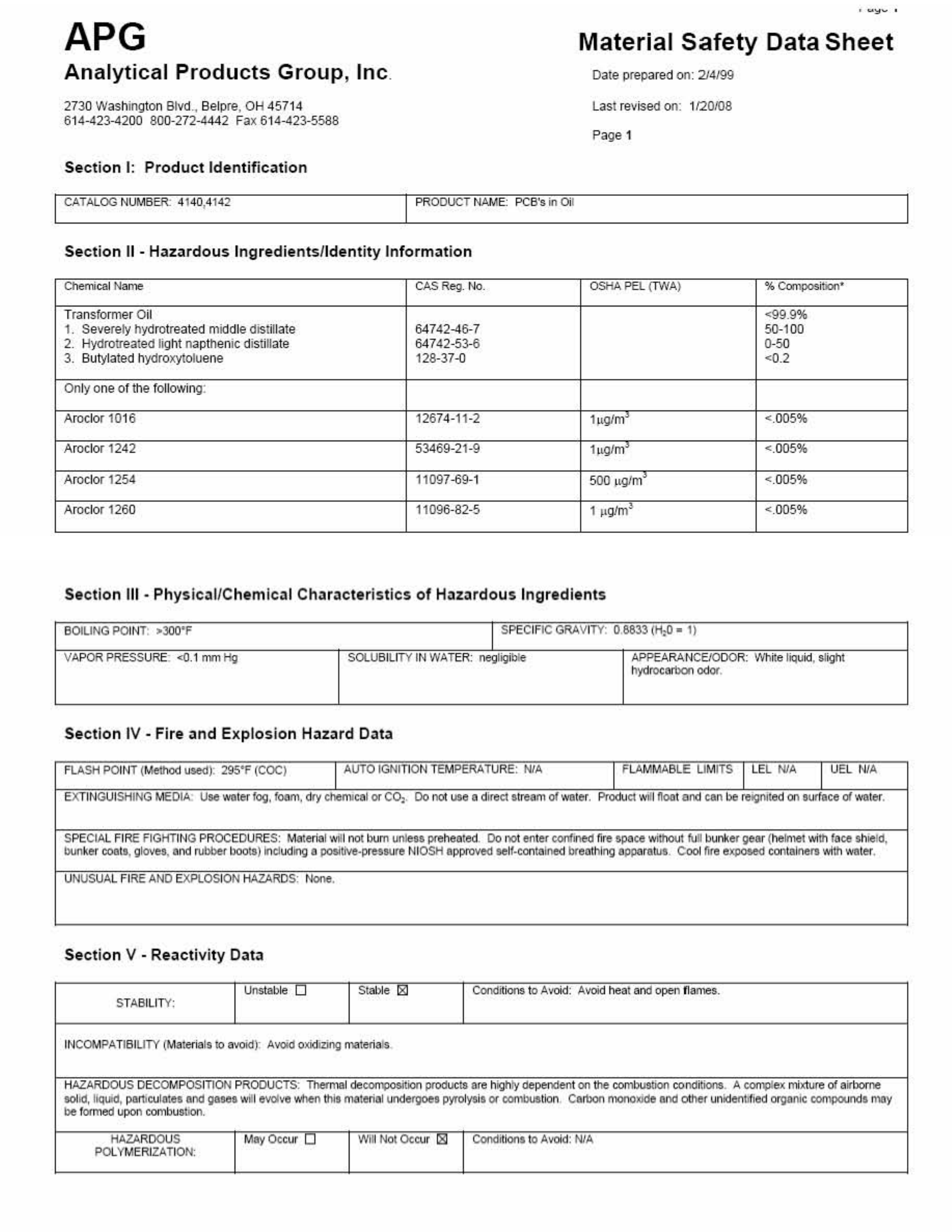
APPENDICES

APPENDIX 1

MATERIALS SAFETY DATA SHEET FOR PCBS IN OIL



APG

Analytical Products Group, Inc.

2730 Washington Blvd., Belpre, OH 45714
614-423-4200 800-272-4442 Fax 614-423-5588

Material Safety Data Sheet

Date prepared on: 2/4/99

Last revised on: 1/20/08

Page 1

Section I: Product Identification

CATALOG NUMBER: 4140,4142	PRODUCT NAME: PCB's in Oil

Section II - Hazardous Ingredients/Identity Information

Chemical Name	CAS Reg. No.	OSHA PEL (TWA)	% Composition*
Transformer Oil 1. Severely hydrotreated middle distillate 2. Hydrotreated light napthenic distillate 3. Butylated hydroxytoluene	 64742-46-7 64742-53-6 128-37-0		<99.9% 50-100 0-50 <0.2
Only one of the following:			
Aroclor 1016	12674-11-2	1μg/m^3	<.005%
Aroclor 1242	53469-21-9	1μg/m^3	<.005%
Aroclor 1254	11097-69-1	500 μg/m^3	<.005%
Aroclor 1260	11096-82-5	1 μg/m^3	<.005%

Section III - Physical/Chemical Characteristics of Hazardous Ingredients

BOILING POINT: >300°F		SPECIFIC GRAVITY: 0.8833 (H_20 = 1)
VAPOR PRESSURE: <0.1 mm Hg	SOLUBILITY IN WATER: negligible	APPEARANCE/ODOR: White liquid, slight hydrocarbon odor.

Section IV - Fire and Explosion Hazard Data

FLASH POINT (Method used): 295°F (COC)	AUTO IGNITION TEMPERATURE: N/A	FLAMMABLE LIMITS	LEL N/A	UEL N/A

EXTINGUISHING MEDIA: Use water fog, foam, dry chemical or CO_2. Do not use a direct stream of water. Product will float and can be reignited on surface of water.

SPECIAL FIRE FIGHTING PROCEDURES: Material will not burn unless preheated. Do not enter confined fire space without full bunker gear (helmet with face shield, bunker coats, gloves, and rubber boots) including a positive-pressure NIOSH approved self-contained breathing apparatus. Cool fire exposed containers with water.

UNUSUAL FIRE AND EXPLOSION HAZARDS: None.

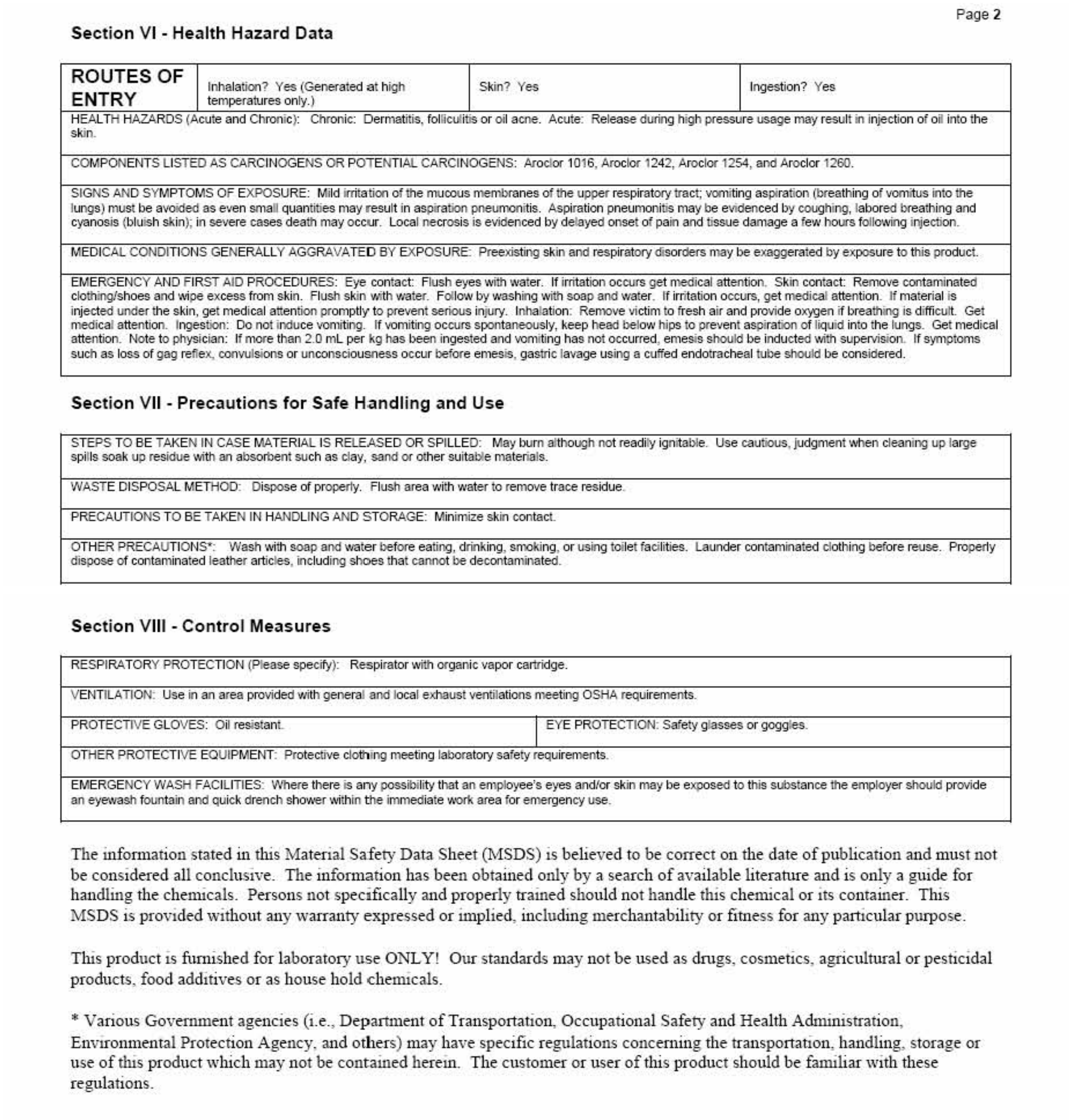
Section V - Reactivity Data

STABILITY:	Unstable ☐	Stable ☒	Conditions to Avoid: Avoid heat and open flames.

INCOMPATIBILITY (Materials to avoid): Avoid oxidizing materials.

HAZARDOUS DECOMPOSITION PRODUCTS: Thermal decomposition products are highly dependent on the combustion conditions. A complex mixture of airborne solid, liquid, particulates and gases will evolve when this material undergoes pyrolysis or combustion. Carbon monoxide and other unidentified organic compounds may be formed upon combustion.

HAZARDOUS POLYMERIZATION:	May Occur ☐	Will Not Occur ☒	Conditions to Avoid: N/A



Section VI - Health Hazard Data

ROUTES OF ENTRY	Inhalation? Yes (Generated at high temperatures only.)	Skin? Yes	Ingestion? Yes

HEALTH HAZARDS (Acute and Chronic): Chronic: Dermatitis, folliculitis or oil acne. Acute: Release during high pressure usage may result in injection of oil into the skin.

COMPONENTS LISTED AS CARCINOGENS OR POTENTIAL CARCINOGENS: Aroclor 1016, Aroclor 1242, Aroclor 1254, and Aroclor 1260.

SIGNS AND SYMPTOMS OF EXPOSURE: Mild irritation of the mucous membranes of the upper respiratory tract; vomiting aspiration (breathing of vomitus into the lungs) must be avoided as even small quantities may result in aspiration pneumonitis. Aspiration pneumonitis may be evidenced by coughing, labored breathing and cyanosis (bluish skin); in severe cases death may occur. Local necrosis is evidenced by delayed onset of pain and tissue damage a few hours following injection.

MEDICAL CONDITIONS GENERALLY AGGRAVATED BY EXPOSURE: Preexisting skin and respiratory disorders may be exaggerated by exposure to this product.

EMERGENCY AND FIRST AID PROCEDURES: Eye contact: Flush eyes with water. If irritation occurs get medical attention. Skin contact: Remove contaminated clothing/shoes and wipe excess from skin. Flush skin with water. Follow by washing with soap and water. If irritation occurs, get medical attention. If material is injected under the skin, get medical attention promptly to prevent serious injury. Inhalation: Remove victim to fresh air and provide oxygen if breathing is difficult. Get medical attention. Ingestion: Do not induce vomiting. If vomiting occurs spontaneously, keep head below hips to prevent aspiration of liquid into the lungs. Get medical attention. Note to physician: If more than 2.0 mL per kg has been ingested and vomiting has not occurred, emesis should be inducted with supervision. If symptoms such as loss of gag reflex, convulsions or unconsciousness occur before emesis, gastric lavage using a cuffed endotracheal tube should be considered.

Section VII - Precautions for Safe Handling and Use

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED: May burn although not readily ignitable. Use cautious, judgment when cleaning up large spills soak up residue with an absorbent such as clay, sand or other suitable materials.

WASTE DISPOSAL METHOD: Dispose of properly. Flush area with water to remove trace residue.

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE: Minimize skin contact.

OTHER PRECAUTIONS*: Wash with soap and water before eating, drinking, smoking, or using toilet facilities. Launder contaminated clothing before reuse. Properly dispose of contaminated leather articles, including shoes that cannot be decontaminated.

Section VIII - Control Measures

RESPIRATORY PROTECTION (Please specify): Respirator with organic vapor cartridge.

VENTILATION: Use in an area provided with general and local exhaust ventilations meeting OSHA requirements.

PROTECTIVE GLOVES: Oil resistant.	EYE PROTECTION: Safety glasses or goggles.

OTHER PROTECTIVE EQUIPMENT: Protective clothing meeting laboratory safety requirements.

EMERGENCY WASH FACILITIES: Where there is any possibility that an employee's eyes and/or skin may be exposed to this substance the employer should provide an eyewash fountain and quick drench shower within the immediate work area for emergency use.

The information stated in this Material Safety Data Sheet (MSDS) is believed to be correct on the date of publication and must not be considered all conclusive. The information has been obtained only by a search of available literature and is only a guide for handling the chemicals. Persons not specifically and properly trained should not handle this chemical or its container. This MSDS is provided without any warranty expressed or implied, including merchantability or fitness for any particular purpose.

This product is furnished for laboratory use ONLY! Our standards may not be used as drugs, cosmetics, agricultural or pesticidal products, food additives or as house hold chemicals.

* Various Government agencies (i.e., Department of Transportation, Occupational Safety and Health Administration, Environmental Protection Agency, and others) may have specific regulations concerning the transportation, handling, storage or use of this product which may not be contained herein. The customer or user of this product should be familiar with these regulations.

APPENDIX 2

STOCKHOLM CONVENTION ON PERSISTENT ORANGIC POLLUTANTS – ANNEX A, PART II

Part11

Polychlorinated Biphenyls

Each party shall:

(a) With regard to the elimination of the use of polychlorinated biphenyls in equipment (e.g. transformers, capacitors or other receptacles containing liquid stocks) by 2025, subject to review by the Conference of the Parties, take action in accordance with the following priorities:

(1) Make determined efforts to identify, label and remove from use equipment containing greater than 10 per cent polychlorinated biphenyls and volumes greater than 5 litres;

(2) Make determined efforts to identify, label and remove from use equipment containing greater than 0.05 per cent polychlorinated biphenyls and greater volumes than 5 litres;

(3) Endeavour to identify and remove use equipment containing greater than 0.005 percent polychlorinated biphenyls and volume greater than 0.05 litres;

(b) Consistent with the priorities in subparagraph (a), promote the following measures to reduce exposures and risks to control the use of polychlorinated biphenyls:

(1) Use only in intact and non-leaking equipment and only in areas where the risk from environmental release can be minimised and quickly remedied;

(2) Not use in equipment in areas associated with the production or processing of food or feed;

(3) When used in populated areas, including schools and hospitals, all reasonable measures to protect from electrical failure which could result in a fire, and regular inspection of equipment for leaks;

(c)Notwithstanding paragraph 2 of Article 3, ensure that equipment containing polychlorinated biphenyls, as described in subparagraph (a), shall not be exported or imported except for the purpose of environmentally sound waste management;

(d) Except for maintenance and servicing operations, not allow recovery for the purpose of reuse in other equipment of liquids with polychlorinated biphenyls content above 0.005 per cent;

(e) Make determined efforts designed to lead to environmentally sound waste management of liquids containing polychlorinated biphenyls and equipment contaminated with polychlorinated biphenyls having polychlorinated biphenyls content above 0.005 per cent, in accordance with paragraph 1 of Article 6, as soon as possible, but no later than 2028, subject to review by the Conference of Parties;

(f) In lieu of note (ii) in Part 1 of this Annex, endeavour to identify other articles containing more than 0.005 per cent polychlorinated biphenyls (e.g. cable-sheaths, cured caulk and painted objects) and manage them in accordance with paragraph 1 of Article 6;

(g) Provide a report every five years on progress in eliminating polychlorinated biphenyls and submit it to the Conference of the Parties pursuant to Article 15;

(h) The reports described in subparagraph (g) shall, as appropriate, be considered by the Conference of the Parties in its reviews to Polychlorinated biphenyls. The Conference of the Parties shall review progress towards elimination of Polychlorinated biphenyls at five year intervals or other period, as appropriate, taking into account such reports.

APPENDIX 3

THE ACTUAL EXECUTION OF THE MATLAB / NETLAB CODE USED FOR THE DEVELOPMENT OF THE NEURAL NETWORK

MATLAB/NETLAB SOURCE CODE FOR TRAINING AND TESTING THE NEURAL NETWORK MODELS OF THE PROCESS OF DECHLORINATION AND THE 164 HOUR OXIDATION TEST

A.3.1 MAIN PROGRAM FOR TRAINING AND TESTING THE NEURAL NETWORK

Below is the source code for training and testing the neural network. However this code uses various other script type functions seen in subsequent sections of this appendix.

```
% Training and Testing a multilayer perceptron neural network
% that models a process of Dechlorination followed by a 164
% hour oxidation test
%
% Description
% The problem consists of building a neural network with 1 input
% x (PCB Conc Prior to Dechlorination (ppm)) and 4 outputs t
% (Post-Dechlorination Sludge (% by mass))
% (After Regeneration Sludge (% by mass))
% (Post-Dechlorination Acidity (mgKOH/g))
% (After Regeneration Acidity (mgKOH/g))

% See also MLP, NETOPT, MLPFWD
%
%   Copyright (c)  (2010)

%________________________Initialise Program______________________%
clear                        % Clear memory
clc                          % Clear the Matlab command window
format long                  % Increase the number of decimal
positions
                             % for more precision

%_____Load Data from the actual physical process into Matlab_____%
Data = xlsread('Book1.xls');
Data = Data(randperm(8),:);
x(:,1) = Data(:,1);          % Input
t(:,1) = Data(:,3);          % Ouputs
t(:,2) = Data(:,4);
t(:,3) = Data(:,6);
t(:,4) = Data(:,7);

%_____________Setup the neural network parameters________________%
nin = 1;                    % Number of inputs.
nhidden = 7;                % Number of hidden units.
nout = 4;                   % Number of outputs.
alpha = 0.01;               % Coefficient of weight-decay prior

%_________Create and initialize network weight vector____________%
net = mlp(nin, nhidden, nout, 'linear', alpha);

options = zeros(1,18);      % Set up vector of options for the
optimiser.
options(1) = 1;             % This provides display of error values.
options(14) = 300;          % Number of training cycles.
```

```
%____Train the Neural Network using the Quasi Newton method______%
[net, options] = netopt(net, options, x, t, 'quasinew');
                            % Could have also used: scg, conjgrad,hmc,
                            % graddesc

%_____________Testing the neural network parameters______________%
y = mlpfwd(net, x);        % The network output
t
y

%_______________________Computing the Error______________________%
error = (t-y)
absolute_value = abs(error);
total = sum(absolute_value);
final_error = total/8
```

A.3.2. FUNCTIONS USED BY THE MAIN PROGRAM

The functions below are provided by the Netlab tool box.

```
function net = mlp(nin, nhidden, nout, outfunc, prior, beta)
%MLP    Create a 2-layer feedforward network.
%
%   Description
%   NET = MLP(NIN, NHIDDEN, NOUT, FUNC) takes the number of inputs,
%   hidden units and output units for a 2-layer feed-forward network,
%   together with a string FUNC which specifies the output unit
%   activation function, and returns a data structure NET. The weights
%   are drawn from a zero mean, unit variance isotropic Gaussian, with
%   varianced scaled by the fan-in of the hidden or output units as
%   appropriate. This makes use of the Matlab function RANDN and so
the
%   seed for the random weight initialization can be  set using
%   RANDN('STATE', S) where S is the seed value.  The hidden units use
%   the TANH activation function.
%
%   The fields in NET are
%     type = 'mlp'
%     nin = number of inputs
%     nhidden = number of hidden units
%     nout = number of outputs
%     nwts = total number of weights and biases
%     actfn = string describing the output unit activation function:
%         'linear'
%         'logistic
%         'softmax'
%     w1 = first-layer weight matrix
%     b1 = first-layer bias vector
%     w2 = second-layer weight matrix
%     b2 = second-layer bias vector
%    Here W1 has dimensions NIN times NHIDDEN, B1 has dimensions 1
times
%   NHIDDEN, W2 has dimensions NHIDDEN times NOUT, and B2 has
dimensions
%   1 times NOUT.
%
%   NET = MLP(NIN, NHIDDEN, NOUT, FUNC, PRIOR), in which PRIOR is a
%   scalar, allows the field NET.ALPHA in the data structure NET to be
%   set, corresponding to a zero-mean isotropic Gaussian prior with
```

```
%   inverse variance with value PRIOR. Alternatively, PRIOR can
consist
%   of a data structure with fields ALPHA and INDEX, allowing
individual
%   Gaussian priors to be set over groups of weights in the network.
Here
%   ALPHA is a column vector in which each element corresponds to a
%   separate group of weights, which need not be mutually exclusive.
The
%   membership of the groups is defined by the matrix INDX in which
the
%   columns correspond to the elements of ALPHA. Each column has one
%   element for each weight in the matrix, in the order defined by the
%   function MLPPAK, and each element is 1 or 0 according to whether
the
%   weight is a member of the corresponding group or not. A utility
%   function MLPPRIOR is provided to help in setting up the PRIOR data
%   structure.
%
%   NET = MLP(NIN, NHIDDEN, NOUT, FUNC, PRIOR, BETA) also sets the
%   additional field NET.BETA in the data structure NET, where beta
%   corresponds to the inverse noise variance.
%
%   See also
%   MLPPRIOR, MLPPAK, MLPUNPAK, MLPFWD, MLPERR, MLPBKP, MLPGRAD
%

%   Copyright (c) Ian T Nabney (1996-2001)

net.type = 'mlp';
net.nin = nin;
net.nhidden = nhidden;
net.nout = nout;
net.nwts = (nin + 1)*nhidden + (nhidden + 1)*nout;

outfns = {'linear', 'logistic', 'softmax'};

if sum(strcmp(outfunc, outfns)) == 0
  error('Undefined output function. Exiting.');
else
  net.outfn = outfunc;
end

if nargin > 4
  if isstruct(prior)
    net.alpha = prior.alpha;
    net.index = prior.index;
  elseif size(prior) == [1 1]
    net.alpha = prior;
  else
    error('prior must be a scalar or a structure');
  end
end

net.w1 = randn(nin, nhidden)/sqrt(nin + 1);
net.b1 = randn(1, nhidden)/sqrt(nin + 1);
net.w2 = randn(nhidden, nout)/sqrt(nhidden + 1);
net.b2 = randn(1, nout)/sqrt(nhidden + 1);

if nargin == 6
```

```
  net.beta = beta;
end
```

The source code below is provided by the Netlab neural network tool box.

```
function [net, options, varargout] = netopt(net, options, x, t, alg);
%NETOPT Optimize the weights in a network model.
%
%   Description
%
%   NETOPT is a helper function which facilitates the training of
%   networks using the general purpose optimizers as well as sampling
%   from the posterior distribution of parameters using general
purpose
%   Markov chain Monte Carlo sampling algorithms. It can be used with
any
%   function that searches in parameter space using error and gradient
%   functions.
%
%   [NET, OPTIONS] = NETOPT(NET, OPTIONS, X, T, ALG) takes a network
%   data structure NET, together with a vector OPTIONS of parameters
%   governing the behaviour of the optimization algorithm, a matrix X
of
%   input vectors and a matrix T of target vectors, and returns the
%   trained network as well as an updated OPTIONS vector. The string
ALG
%   determines which optimization algorithm (CONJGRAD, QUASINEW, SCG,
%   etc.) or Monte Carlo algorithm (such as HMC) will be used.
%
%   [NET, OPTIONS, VARARGOUT] = NETOPT(NET, OPTIONS, X, T, ALG) also
%   returns any additional return values from the optimisation
algorithm.
%
%   See also
%   NETGRAD, BFGS, CONJGRAD, GRADDESC, HMC, SCG
%

%   Copyright (c) Ian T Nabney (1996-2001)

optstring = [alg, '(''neterr'', w, options, ''netgrad'', net, x, t)'];

% Extract weights from network as single vector
w = netpak(net);

% Carry out optimisation
[s{1:nargout}] = eval(optstring);
w = s{1};

if nargout > 1
  options = s{2};

  % If there are additional arguments, extract them
  nextra = nargout - 2;
  if nextra > 0
    for i = 1:nextra
      varargout{i} = s{i+2};
    end
  end
```

```
end

% Pack the weights back into the network
net = netunpak(net, w);


function w = netpak(net)
%NETPAK Combines weights and biases into one weights vector.
%
%   Description
%   W = NETPAK(NET) takes a network data structure NET and combines
the
%   component weight matrices  into a single row vector W. The
facility
%   to switch between these two representations for the network
%   parameters is useful, for example, in training a network by error
%   function minimization, since a single vector of parameters can be
%   handled by general-purpose optimization routines.  This function
also
%   takes into account a MASK defined as a field in NET by removing
any
%   weights that correspond to entries of 0 in the mask.
%
%   See also
%   NET, NETUNPAK, NETFWD, NETERR, NETGRAD
%

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pakstr = [net.type, 'pak'];
w = feval(pakstr, net);
% Return masked subset of weights
if (isfield(net, 'mask'))
   w = w(logical(net.mask));
end



function [y, z, a] = mlpfwd(net, x)
%MLPFWD Forward propagation through 2-layer network.
%
%   Description
%   Y = MLPFWD(NET, X) takes a network data structure NET together
with a
%   matrix X of input vectors, and forward propagates the inputs
through
%   the network to generate a matrix Y of output vectors. Each row of
X
%   corresponds to one input vector and each row of Y corresponds to
one
%   output vector.
%
%   [Y, Z] = MLPFWD(NET, X) also generates a matrix Z of the hidden
unit
%   activations where each row corresponds to one pattern.
%
%   [Y, Z, A] = MLPFWD(NET, X) also returns a matrix A  giving the
summed
%   inputs to each output unit, where each row corresponds to one
%   pattern.
```

```
%
%   See also
%   MLP, MLPPAK, MLPUNPAK, MLPERR, MLPBKP, MLPGRAD
%

%   Copyright (c) Ian T Nabney (1996-2001)

% Check arguments for consistency
errstring = consist(net, 'mlp', x);
if ~isempty(errstring);
  error(errstring);
end

ndata = size(x, 1);

z = tanh(x*net.w1 + ones(ndata, 1)*net.b1);
a = z*net.w2 + ones(ndata, 1)*net.b2;

switch net.outfn

  case 'linear'    % Linear outputs

    y = a;

  case 'logistic'  % Logistic outputs
    % Prevent overflow and underflow: use same bounds as mlperr
    % Ensure that log(1-y) is computable: need exp(a) > eps
    maxcut = -log(eps);
    % Ensure that log(y) is computable
    mincut = -log(1/realmin - 1);
    a = min(a, maxcut);
    a = max(a, mincut);
    y = 1./(1 + exp(-a));

  case 'softmax'   % Softmax outputs

    % Prevent overflow and underflow: use same bounds as glmerr
    % Ensure that sum(exp(a), 2) does not overflow
    maxcut = log(realmax) - log(net.nout);
    % Ensure that exp(a) > 0
    mincut = log(realmin);
    a = min(a, maxcut);
    a = max(a, mincut);
    temp = exp(a);
    y = temp./(sum(temp, 2)*ones(1, net.nout));

  otherwise
    error(['Unknown activation function ', net.outfn]);
end
```

APPENDIX 4

RESULTS OF THE MATLAB / NETLABCODE EXECUTION FROM APPENDIX 3

The following shows the contents of this Matlab display window as the code above is executed. More specifically, each training cycles can be seen together with the error after each cycle. Also, the testing results are displayed with a condensed error values.

```
Cycle    1  Function    5.795902
Cycle    1  Error    4.354850
Cycle    2  Error    4.354850
Cycle    3  Error    4.354850
Cycle    4  Error    4.006677
Cycle    5  Error    4.006677
Cycle    2  Function    4.006677
Cycle    3  Function    4.005965
Cycle    1  Error    2.973319
Cycle    2  Error    2.973319
Cycle    3  Error    2.941065
Cycle    4  Function    2.941065
Cycle    1  Error    2.785442
Cycle    2  Error    2.710528
Cycle    3  Error    2.710528
Cycle    5  Function    2.710528
Cycle    1  Error    2.686696
Cycle    2  Error    2.686696
Cycle    3  Error    2.686275
Cycle    6  Function    2.686275
Cycle    1  Error    2.669033
Cycle    7  Function    2.669033
Cycle    8  Function    2.668626
Warning: search direction uphill in quasinew
> In quasinew at 118
  In netopt at 36
  In PCBWork_Latest at 46
Cycle    1  Error    2.667254
Cycle    2  Error    2.667254
Cycle    3  Error    2.667244
Cycle    4  Error    2.667243
Cycle    5  Error    2.667243
```

```
Cycle   9  Function    2.667243
Cycle  10  Function    2.603167
Cycle   1  Error    2.396105
Cycle   2  Error    2.396105
Cycle   3  Error    2.380540
Cycle   4  Error    2.379581
Cycle   5  Error    2.379326
Cycle   6  Error    2.379300
Cycle  11  Function    2.379300
Cycle   1  Error    2.271134
Cycle   2  Error    2.271134
Cycle   3  Error    2.269511
Cycle   4  Error    2.269487
Cycle   5  Error    2.269484
Cycle  12  Function    2.269484
Cycle  13  Function    1.906944
Cycle   1  Error    1.831479
Cycle   2  Error    1.831479
Cycle   3  Error    1.830936
Cycle   4  Error    1.830910
Cycle  14  Function    1.830910
Cycle   1  Error    1.733319
Cycle   2  Error    1.733319
Cycle   3  Error    1.733319
Cycle   4  Error    1.733319
Cycle   5  Error    1.733066
Cycle   6  Error    1.733055
Cycle  15  Function    1.733055
Cycle   1  Error    1.728296
Cycle   2  Error    1.728296
Cycle  16  Function    1.728296
Cycle   1  Error    1.680870
Cycle   2  Error    1.680870
Cycle   3  Error    1.680650
Cycle   4  Error    1.680646
Cycle  17  Function    1.680646
Cycle  18  Function    1.633201
```

```
Cycle   19  Function    1.589791
Cycle   20  Function    1.568092
Cycle   21  Function    1.550816
Cycle   22  Function    1.535222
Cycle   23  Function    1.505045
Cycle   24  Function    1.485032
Cycle   25  Function    1.472129
Cycle   26  Function    1.440930
Cycle   27  Function    1.426709
Cycle   28  Function    1.409604
Cycle   29  Function    1.392256
Cycle   30  Function    1.388125
Cycle   31  Function    1.385675
Cycle   32  Function    1.373863
Cycle   33  Function    1.368144
Cycle   34  Function    1.356132
Cycle   35  Function    1.339751
Cycle    1  Error    1.324889
Cycle    2  Error    1.324889
Cycle    3  Error    1.324840
Cycle    4  Error    1.324836
Cycle    5  Error    1.324836
Cycle   36  Function    1.324836
Cycle    1  Error    1.320577
Cycle    2  Error    1.320577
Cycle    3  Error    1.320577
Cycle    4  Error    1.320561
Cycle    5  Error    1.320561
Cycle   37  Function    1.320561
Cycle   38  Function    1.305792
Cycle    1  Error    1.296277
Cycle    2  Error    1.296277
Cycle    3  Error    1.296241
Cycle    4  Error    1.296236
Cycle    5  Error    1.296236
Cycle    6  Error    1.296236
Cycle   39  Function    1.296236
```

```
Cycle  40  Function   1.286337
Cycle  41  Function   1.272731
Cycle  42  Function   1.266034
Cycle  43  Function   1.260898
Cycle  44  Function   1.254669
Cycle  45  Function   1.247993
Cycle  46  Function   1.235090
Cycle  47  Function   1.224428
Cycle   1  Error   1.213738
Cycle   2  Error   1.213738
Cycle   3  Error   1.213738
Cycle   4  Error   1.213738
Cycle  48  Function   1.213738
Cycle  49  Function   1.211173
Cycle  50  Function   1.211134
Cycle   1  Error   1.204068
Cycle   2  Error   1.204068
Cycle   3  Error   1.203928
Cycle  51  Function   1.203928
Cycle   1  Error   1.182482
Cycle   2  Error   1.182482
Cycle   3  Error   1.182182
Cycle   4  Error   1.182182
Cycle   5  Error   1.182182
Cycle  52  Function   1.182182
Cycle  53  Function   1.172914
Cycle   1  Error   1.163927
Cycle   2  Error   1.163927
Cycle   3  Error   1.162785
Cycle   4  Error   1.162772
Cycle   5  Error   1.162745
Cycle   6  Error   1.162745
Cycle  54  Function   1.162745
Cycle   1  Error   1.158073
Cycle   2  Error   1.158073
Cycle   3  Error   1.158030
Cycle   4  Error   1.158007
```

```
Cycle    5  Error    1.158007
Cycle    6  Error    1.158003
Cycle   55  Function    1.158003
Cycle    1  Error    1.153601
Cycle    2  Error    1.153601
Cycle    3  Error    1.153364
Cycle   56  Function    1.153364
Cycle   57  Function    1.142339
Cycle   58  Function    1.130855
Cycle    1  Error    1.122687
Cycle    2  Error    1.122687
Cycle    3  Error    1.122305
Cycle    4  Error    1.122305
Cycle    5  Error    1.122305
Cycle    6  Error    1.122305
Cycle    7  Error    1.122305
Cycle   59  Function    1.122305
Cycle   60  Function    1.108962
Cycle   61  Function    1.095124
Cycle   62  Function    1.088689
Cycle    1  Error    1.072751
Cycle    2  Error    1.072751
Cycle    3  Error    1.072659
Cycle    4  Error    1.072658
Cycle    5  Error    1.072657
Cycle   63  Function    1.072657
Cycle    1  Error    1.063453
Cycle    2  Error    1.063453
Cycle    3  Error    1.062927
Cycle    4  Error    1.062927
Cycle    5  Error    1.062927
Cycle    6  Error    1.062927
Cycle    7  Error    1.062927
Cycle    8  Error    1.062927
Cycle   64  Function    1.062927
Cycle   65  Function    1.060623
Cycle   66  Function    1.042949
```

```
Cycle   1  Error    1.038309
Cycle   2  Error    1.038309
Cycle   3  Error    1.038274
Cycle   4  Error    1.038273
Cycle   5  Error    1.038273
Cycle   6  Error    1.038273
Cycle   7  Error    1.038273
Cycle  67  Function    1.038273
Cycle  68  Function    1.031595
Cycle   1  Error    1.023674
Cycle   2  Error    1.023674
Cycle   3  Error    1.023663
Cycle   4  Error    1.023662
Cycle  69  Function    1.023662
Cycle   1  Error    1.013945
Cycle   2  Error    1.013945
Cycle   3  Error    1.013945
Cycle   4  Error    1.013945
Cycle   5  Error    1.013945
Cycle   6  Error    1.013945
Cycle  70  Function    1.013945
Cycle   1  Error    1.006358
Cycle   2  Error    1.006358
Cycle   3  Error    1.005898
Cycle   4  Error    1.005898
Cycle   5  Error    1.005898
Cycle   6  Error    1.005898
Cycle   7  Error    1.005898
Cycle  71  Function    1.005898
Cycle   1  Error    1.004095
Cycle   2  Error    1.004095
Cycle   3  Error    1.004018
Cycle   4  Error    1.004018
Cycle   5  Error    1.004018
Cycle   6  Error    1.004018
Cycle  72  Function    1.004018
Cycle  73  Function    1.000503
```

```
Cycle   74  Function    0.991846
Cycle    1  Error    0.981656
Cycle    2  Error    0.981656
Cycle    3  Error    0.981400
Cycle    4  Error    0.981398
Cycle    5  Error    0.981397
Cycle    6  Error    0.981397
Cycle    7  Error    0.981397
Cycle   75  Function    0.981397
Cycle   76  Function    0.968075
Cycle    1  Error    0.961565
Cycle    2  Error    0.961565
Cycle    3  Error    0.961484
Cycle    4  Error    0.961483
Cycle    5  Error    0.961483
Cycle   77  Function    0.961483
Cycle   78  Function    0.952922
Cycle   79  Function    0.917504
Cycle    1  Error    0.897789
Cycle    2  Error    0.897789
Cycle    3  Error    0.897205
Cycle    4  Error    0.897196
Cycle   80  Function    0.897196
Cycle    1  Error    0.868723
Cycle    2  Error    0.868723
Cycle    3  Error    0.868584
Cycle    4  Error    0.868558
Cycle   81  Function    0.868558
Cycle    1  Error    0.833054
Cycle    2  Error    0.833054
Cycle    3  Error    0.832297
Cycle    4  Error    0.832252
Cycle    5  Error    0.832239
Cycle   82  Function    0.832239
Cycle   83  Function    0.774417
Cycle   84  Function    0.734052
Cycle    1  Error    0.708009
```

```
Cycle   2  Error    0.708009
Cycle   3  Error    0.707973
Cycle   4  Error    0.707972
Cycle   5  Error    0.707972
Cycle  85  Function    0.707972
Cycle   1  Error    0.694137
Cycle   2  Error    0.694137
Cycle   3  Error    0.693959
Cycle   4  Error    0.693959
Cycle   5  Error    0.693959
Cycle   6  Error    0.693959
Cycle   7  Error    0.693959
Cycle  86  Function    0.693959
Cycle   1  Error    0.681622
Cycle   2  Error    0.681622
Cycle   3  Error    0.681477
Cycle   4  Error    0.681476
Cycle   5  Error    0.681476
Cycle  87  Function    0.681476
Cycle  88  Function    0.656776
Cycle  89  Function    0.626597
Cycle  90  Function    0.606745
Cycle  91  Function    0.593834
Cycle  92  Function    0.583349
Cycle   1  Error    0.573892
Cycle   2  Error    0.573892
Cycle   3  Error    0.573420
Cycle   4  Error    0.573420
Cycle   5  Error    0.573420
Cycle   6  Error    0.573420
Cycle   7  Error    0.573420
Cycle   8  Error    0.573420
Cycle  93  Function    0.573420
Cycle  94  Function    0.566499
Cycle  95  Function    0.561232
Cycle  96  Function    0.553769
Cycle  97  Function    0.545610
```

```
Cycle   98  Function    0.537055
Cycle    1  Error    0.532451
Cycle    2  Error    0.532451
Cycle    3  Error    0.532191
Cycle    4  Error    0.532191
Cycle    5  Error    0.532191
Cycle    6  Error    0.532191
Cycle   99  Function    0.532191
Cycle  100  Function    0.525425
Cycle  101  Function    0.519376
Cycle  102  Function    0.512658
Cycle  103  Function    0.511511
Cycle  104  Function    0.500185
Cycle  105  Function    0.494010
Cycle  106  Function    0.484444
Cycle  107  Function    0.472564
Cycle  108  Function    0.460538
Cycle    1  Error    0.455512
Cycle    2  Error    0.455512
Cycle    3  Error    0.455399
Cycle    4  Error    0.455390
Cycle    5  Error    0.455389
Cycle    6  Error    0.455389
Cycle    7  Error    0.455389
Cycle  109  Function    0.455389
Cycle  110  Function    0.453227
Cycle    1  Error    0.438967
Cycle    2  Error    0.438967
Cycle    3  Error    0.438279
Cycle    4  Error    0.438274
Cycle    5  Error    0.438273
Cycle    6  Error    0.438273
Cycle  111  Function    0.438273
Cycle    1  Error    0.430780
Cycle    2  Error    0.430312
Cycle    3  Error    0.430093
Cycle    4  Error    0.430093
```

```
Cycle    5  Error    0.430093
Cycle  112  Function    0.430093
Cycle  113  Function    0.429941
Cycle  114  Function    0.421453
Cycle  115  Function    0.419470
Cycle  116  Function    0.416670
Cycle  117  Function    0.410070
Cycle  118  Function    0.405908
Cycle  119  Function    0.398531
Cycle  120  Function    0.394424
Cycle  121  Function    0.387521
Cycle  122  Function    0.378089
Cycle  123  Function    0.374901
Cycle    1  Error    0.370546
Cycle    2  Error    0.370349
Cycle    3  Error    0.370189
Cycle    4  Error    0.370189
Cycle    5  Error    0.370189
Cycle  124  Function    0.370189
Cycle  125  Function    0.363733
Cycle  126  Function    0.359775
Cycle  127  Function    0.351851
Cycle  128  Function    0.343722
Cycle  129  Function    0.335297
Cycle    1  Error    0.332313
Cycle    2  Error    0.332313
Cycle    3  Error    0.332275
Cycle    4  Error    0.332273
Cycle    5  Error    0.332273
Cycle    6  Error    0.332273
Cycle    7  Error    0.332273
Cycle  130  Function    0.332273
Cycle  131  Function    0.326297
Cycle  132  Function    0.320018
Cycle  133  Function    0.314744
Cycle  134  Function    0.311542
Cycle  135  Function    0.307697
```

```
Cycle  136  Function    0.303136
Cycle  137  Function    0.301165
Cycle  138  Function    0.297393
Cycle  139  Function    0.293944
Cycle  140  Function    0.289907
Cycle  141  Function    0.284394
Cycle  142  Function    0.280722
Cycle  143  Function    0.277346
Cycle  144  Function    0.276157
Cycle  145  Function    0.274130
Cycle  146  Function    0.271778
Cycle  147  Function    0.270624
Cycle  148  Function    0.270120
Cycle  149  Function    0.268842
Cycle  150  Function    0.266792
Cycle  151  Function    0.264418
Cycle  152  Function    0.262596
Cycle  153  Function    0.262221
Cycle  154  Function    0.260775
Cycle  155  Function    0.260477
Cycle  156  Function    0.260042
Cycle  157  Function    0.259320
Cycle  158  Function    0.259131
Cycle  159  Function    0.258795
Cycle  160  Function    0.258545
Cycle  161  Function    0.258276
Cycle  162  Function    0.258078
Cycle  163  Function    0.257924
Cycle  164  Function    0.257750
Cycle  165  Function    0.257578
Cycle  166  Function    0.257458
Cycle  167  Function    0.257365
Cycle  168  Function    0.257250
Cycle  169  Function    0.257076
Cycle  170  Function    0.256912
Cycle  171  Function    0.256797
Cycle  172  Function    0.256694
```

```
Cycle  173  Function    0.256569
Cycle  174  Function    0.256378
Cycle  175  Function    0.256182
Cycle  176  Function    0.256015
Cycle  177  Function    0.255840
Cycle  178  Function    0.255544
Cycle  179  Function    0.255096
Cycle  180  Function    0.254605
Cycle  181  Function    0.254268
Cycle  182  Function    0.254102
Cycle  183  Function    0.253797
Cycle  184  Function    0.253314
Cycle  185  Function    0.252724
Cycle  186  Function    0.251494
Cycle  187  Function    0.250657
Cycle  188  Function    0.250283
Cycle  189  Function    0.249606
Cycle  190  Function    0.249256
Cycle  191  Function    0.248575
Cycle  192  Function    0.248317
Cycle  193  Function    0.247878
Cycle  194  Function    0.247433
Cycle  195  Function    0.246933
Cycle  196  Function    0.246402
Cycle  197  Function    0.245843
Cycle  198  Function    0.245550
Cycle  199  Function    0.245112
Cycle  200  Function    0.244811
Cycle  201  Function    0.244623
Cycle  202  Function    0.244481
Cycle  203  Function    0.244389
Cycle  204  Function    0.244244
Cycle  205  Function    0.244104
Cycle  206  Function    0.243800
Cycle  207  Function    0.243460
Cycle  208  Function    0.243194
Cycle  209  Function    0.243043
```

```
Cycle  210  Function    0.242921
Cycle  211  Function    0.242781
Cycle  212  Function    0.242619
Cycle  213  Function    0.242489
Cycle  214  Function    0.242407
Cycle  215  Function    0.242357
Cycle  216  Function    0.242310
Cycle  217  Function    0.242262
Cycle  218  Function    0.242221
Cycle  219  Function    0.242181
Cycle  220  Function    0.242154
Cycle  221  Function    0.242128
Cycle  222  Function    0.242095
Cycle  223  Function    0.242051
Cycle  224  Function    0.242016
Cycle  225  Function    0.242001
Cycle  226  Function    0.241994
Cycle  227  Function    0.241987
Cycle  228  Function    0.241970
Cycle  229  Function    0.241941
Cycle  230  Function    0.241903
Cycle  231  Function    0.241878
Cycle  232  Function    0.241867
Cycle  233  Function    0.241863
Cycle  234  Function    0.241858
Cycle  235  Function    0.241846
Cycle  236  Function    0.241826
Cycle  237  Function    0.241793
Cycle  238  Function    0.241761
Cycle  239  Function    0.241743
Cycle  240  Function    0.241737
Cycle  241  Function    0.241734
Cycle  242  Function    0.241729
Cycle  243  Function    0.241718
Cycle  244  Function    0.241704
Cycle  245  Function    0.241692
Cycle  246  Function    0.241682
```

```
Cycle  247  Function    0.241674
Cycle  248  Function    0.241660
Cycle  249  Function    0.241635
Cycle  250  Function    0.241599
Cycle  251  Function    0.241562
Cycle  252  Function    0.241544
Cycle  253  Function    0.241536
Cycle  254  Function    0.241528
Cycle  255  Function    0.241517
Cycle  256  Function    0.241494
Cycle  257  Function    0.241448
Cycle  258  Function    0.241363
Cycle  259  Function    0.241218
Cycle  260  Function    0.241026
Cycle  261  Function    0.240755
Cycle  262  Function    0.240412
Cycle    1  Error    0.240300
Cycle    2  Error    0.240300
Cycle    3  Error    0.240296
Cycle    4  Error    0.240296
Cycle    5  Error    0.240296
Cycle    6  Error    0.240296
Cycle    7  Error    0.240296
Cycle  263  Function    0.240296
Cycle  264  Function    0.240250
Cycle  265  Function    0.240224
Cycle  266  Function    0.240213
Cycle  267  Function    0.240194
Cycle  268  Function    0.240168
Cycle  269  Function    0.240111
Cycle  270  Function    0.240060
Cycle  271  Function    0.240028
Cycle  272  Function    0.240013
Cycle  273  Function    0.239991
Cycle  274  Function    0.239975
Cycle  275  Function    0.239963
Cycle  276  Function    0.239957
```

```
Cycle  277  Function    0.239955
Cycle  278  Function    0.239952
Cycle  279  Function    0.239947
Cycle  280  Function    0.239939
Cycle  281  Function    0.239930
Cycle  282  Function    0.239925
Cycle  283  Function    0.239924
Cycle  284  Function    0.239924
Cycle  285  Function    0.239924
Cycle  286  Function    0.239924
Cycle  287  Function    0.239924
Cycle  288  Function    0.239924
Cycle  289  Function    0.239924
Cycle  290  Function    0.239923
Cycle  291  Function    0.239923
Cycle  292  Function    0.239923
Cycle  293  Function    0.239923
Cycle  294  Function    0.239923
Cycle  295  Function    0.239923
Cycle  296  Function    0.239923
Cycle  297  Function    0.239923
Cycle  298  Function    0.239923
Cycle  299  Function    0.239923
Cycle  300  Function    0.239923
Maximum number of iterations has been exceeded

t =

   1.650000000000000   0.780000000000000   1.460000000000000   1.580000000000000
   1.870000000000000   0.630000000000000   1.770000000000000   1.250000000000000
   2.300000000000000   1.400000000000000   3.020000000000000   1.620000000000000
   0.920000000000000   0.500000000000000   1.560000000000000   0.880000000000000
   1.310000000000000   0.260000000000000   1.190000000000000   0.740000000000000
   2.060000000000000   1.060000000000000   2.500000000000000   1.130000000000000
   0.420000000000000   0.540000000000000   1.140000000000000   0.720000000000000
   0.710000000000000   0.680000000000000   1.230000000000000   0.650000000000000
```

```
y =

   1.759094808230166   0.686398005836463   1.605821131584036   1.394713359902200
   1.752212109430362   0.702355898933282   1.616141601401630   1.413695601223982
   2.392791423509879   1.386705807227279   3.007962545612929   1.522217673208337
   1.011053216787444   0.510037735056904   1.586914556357650   0.838683644624587
   1.299495289439456   0.299751111700375   1.194129418333201   0.763025740520823
   1.884872594982724   1.065925328287480   2.490023320887617   1.269296279218797
   0.411277229138223   0.554678126984988   1.135269752523392   0.710715166298223
   0.724854816074746   0.642511093148704   1.227490667186088   0.653635579373963


error =

  -0.109094808230166   0.093601994163537  -0.145821131584036   0.185286640097800
   0.117787890569638  -0.072355898933282   0.153858398598370  -0.163695601223982
  -0.092791423509879   0.013294192772721   0.012037454387071   0.097782326791663
  -0.091053216787443  -0.010037735056904  -0.026914556357650   0.041316355375413
   0.010504710560544  -0.039751111700375  -0.004129418333201  -0.023025740520823
   0.175127405017276  -0.005925328287480   0.009976679112383  -0.139296279218797
   0.008722770861777  -0.014678126984988   0.004730247476608   0.009284833701777
  -0.014854816074746   0.037488906851296   0.002509332813912  -0.003635579373963


final_error =

   0.077492130201434   0.035891661843823   0.044997152332904   0.082915419538027

>> net

net =

       type: 'mlp'
        nin: 1
    nhidden: 7
       nout: 4
```

```
     nwts: 46
    outfn: 'linear'
    alpha: 0.010000000000000
       w1: [1x7 double]
       b1: [1x7 double]
       w2: [7x4 double]
       b2:          [0.435227020959160          0.163629790983202          0.623837556387389
0.400759176289016]
```