



UNIVERSITI PUTRA MALAYSIA

**ELECTROCHEMICAL ACTIVATION PROCESS FOR TREATING
HIGH STRENGTH WASTE**

YAP SIEW YEIN

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**ELECTROCHEMICAL ACTIVATION PROCESS FOR TREATING HIGH
STRENGTH WASTE**

By

YAP SIEW YEIN

**Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of
Science in the Faculty of Engineering
Universiti Putra Malaysia**

May 2001



Dedicated to daddy,

For your love and all you have done for the family



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

ELECTROCHEMICAL ACTIVATION PROCESS FOR TREATING HIGH STRENGTH WASTE

By

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May 2001

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Electrochemical Activation Process (ECA) is a method whereby electrical current is introduced to induce a chemical reaction in water containing natural salts. As a result, this process will produce a substantial electrical potential difference, leading to the generation of anolyte and catholyte. The anolyte generated by the STEL®-ECA unit system were found to contain Cl_2 , Cl^- , HClO , HCl , ClO_2 , O_2 , O_3 , and H_2O_2 . As for catholyte, analyses using the ICP and IR spectroscopy showed that it contains the hydroxides of sodium, potassium, magnesium and calcium. Besides, kinetic studies on the decomposition of the components in anolyte were also studied.

Both activated solutions, anolyte and catholyte were used to treat passivation waste and landfill leachate. The studies include using anolyte and catholyte in COD reduction, the effect of contact time (of anolyte and the waste) on COD reduction, kinetics of the reaction between anolyte and the waste, using of catholyte in coagulation and



flocculation, biodegradability of the waste after treatment and others. Finally, a case study was carried out to investigate the possibility of using anolyte in combination with other treatment methods, for example, aerobic, anaerobic, sedimentation and absorption to treat chemical waste. The physical-chemical-biological treatment reactor designed for the treatment of chemical waste was closely monitored for 143 days on its COD, BOD and biodegradability.

For passivation waste, COD removal was 70% using anolyte for at least 24 hours of contact time. High efficiency on the formation and settling of floc were observed when catholyte is used together with alum and anionic polymer. In addition, the non-readily biodegradable waste was transformed to a more readily biodegradable waste after at least a 24 hours reaction with the activated solutions. As for leachate, anolyte showed good reduction in COD and ammoniacal nitrogen, whereas catholyte showed good reduction in ferum and zinc. Finally, data obtained from the case study showed that anolyte is able to convert a non-readily biodegradable waste to a more readily biodegradable waste.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PROSES ELEKTROKIMIA AKTIF UNTUK MERAWAT SISA KUAT

Oleh

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Proses Elektrokimia Aktif adalah suatu proses dimana arus elektrik dibekalkan untuk merangsangkan suatu tindakbalas kimia di dalam suatu larutan bergaram. Proses ini menyebabkan suatu perubahan keupayaan elektrik lalu menghasilkan larutan 'anolyte' dan 'catholyte'. 'Anolyte' yang dijanakan oleh sistem unit STEL®-ECA didapati mengandungi Cl_2 , Cl^- , HClO , HCl , ClO_2 , O_2 , O_3 , dan H_2O_2 . Untuk 'catholyte' pula, analisis menggunakan spektroskopi ICP dan IR menunjukkan bahawa ia mengandungi hidroksida natrium, kalium, magnesium dan kalsium. Selain itu, kinetik perlesapan komponen dalam 'anolyte' turut dikaji.

Kedua-dua larutan aktif, 'anolyte' dan 'catholyte' telah digunakan untuk merawat sisa pasif dan air sisa dari tempat pembuangan sampah. Kajian ini termasuk penentuan dos terbaik 'anolyte' dan 'catholyte' dalam penurunan COD, kesan masa sentuhan antara 'anolyte' dengan sisa terhadap penurunan COD, kinetik tindakbalas antara 'anolyte'

dengan sisa, penggunaan 'catholyte' dalam proses penggumpalan, biodegradasi sisa selepas rawatan dan sebagainya. Akhirnya, suatu kajian kes dijalankan untuk mengkaji pergabungan 'anolyte' dengan kaedah rawatan lain seperti aerobik, anaerobik, pemendapan dan penyerapan untuk merawat sisa kimia. Reaktor rawatan fizikal-kimia-biologi rekaan itu telah dijalankan selama 143 hari dan parameter COD, BOD dan kebolehan sisa dibiodegradasikan telahpun dikaji.

Untuk sisa pasif, penurunan COD yang dicapai adalah sebanyak 70% apabila 'anolyte' digunakan dengan masa tindakbalas sekurang-kurangnya 24 jam. Penggunaan 'catholyte' bersama-sama dengan alum dan polimer anionik telah menunjukkan keberkesanan yang tinggi dalam pembentukan 'floc' dan pemendapan 'floc'. Selain itu, sisa yang pada mulanya tidak terbiodegradasi, telah menjadi terbiodegradasi selepas rawatan dengan larutan-larutan aktif itu. Untuk 'leachate' pula, 'anolyte' menunjukkan keputusan yang baik dalam penurunan COD dan nitrogen ammonia manakala 'catholyte' pula menunjukkan keputusan yang baik dalam penurunan ferum dan zink. Akhirnya, data yang diperolehi dari kajian kes menunjukkan bahawa 'anolyte' berkebolehan menukarkan sisa tidak terbiodegradasi kepada sisa terbiodegradasi.

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I certify that an Examination Committee met on 14th May 2001 to conduct the final examination of Yap Siew Yein on her Master of Science thesis entitled "Electrochemical Activation Process For Treating High Strength Waste" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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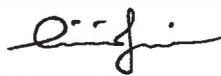
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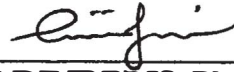


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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



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TABLE OF CONTENTS

| | Page |
|---|------|
| DEDICATION | ii |
| ABSTRACT | iii |
| ABSTRAK | v |
| ACKNOWLEDGEMENTS | vii |
| APPROVAL SHEETS | viii |
| DECLARATION FORM | x |
| LIST OF TABLES | xiv |
| LIST OF FIGURES | xvi |
| LIST OF ABBREVIATIONS | xix |
| | |
| CHAPTER | |
| | |
| 1 INTRODUCTION | 1 |
| 1.1 General | 1 |
| 1.2 Electrochemical Activation (ECA) | 2 |
| 1.3 Flow-Through Electrochemical Modular (FEM) | 3 |
| 1.4 The STEL® ECA System | 5 |
| 1.4.1 Space Age Technology | 5 |
| 1.4.2 Characteristics of the STEL® ECA System | 5 |
| 1.4.3 Basic Principal of the STEL® unit | 7 |
| 1.5 Anolyte | 11 |
| 1.6 Catholyte | 14 |
| 1.7 Study using ECA Solutions (Anolyte and Catholyte) for Treating High Strength Waste | 15 |
| 1.8 Objectives | 16 |
| 1.9 Research Outline | 17 |
| | |
| 2 LITERATURE REVIEW | 18 |
| 2.1 The Evolution of ECA System | 19 |
| 2.2 ECA in Medicine and Biology | 24 |
| 2.2.1 ECA Solutions As Antiseptic Agents and Biological Active Solutions for Treating Diseases | 25 |
| 2.2.2 ECA Solutions As Washing, Disinfectant and Sterilant Solution | 28 |
| 2.3 ECA in Agriculture | 33 |
| 2.4 ECA in Industry | 36 |
| 2.5 Other Research and Studies (Outside Russia) Using Electrochemical Method for Treating Wastewater | 41 |



| | | |
|---------|--|-----|
| 3 | STUDIES USING ECA ACTIVATED SOLUTIONS FOR TREATING RECALCITRANT WASTE | |
| 3.1 | Study on the Characteristics of the Activated Solutions Generated | 46 |
| 3.1.1 | Experimental Methods | 46 |
| 3.1.1.1 | Experimental Set-Up | 47 |
| 3.1.1.2 | Maintenance | 48 |
| 3.1.1.3 | Functions of the STEL® and its Generated Activated Solutions | 49 |
| 3.1.2 | Results and Discussion | 52 |
| 3.1.2.1 | Functions of the STEL® | 52 |
| 3.1.2.2 | Characterization of Anolyte and Catholyte | 56 |
| 3.1.3 | Summary | 66 |
| 3.2 | Activated Solutions In Treating Passivation Waste | 67 |
| 3.2.1 | Experimental Methods | 67 |
| 3.2.1.1 | Characteristics of the Passivation Waste | 67 |
| 3.2.1.2 | Anolyte and Catholyte Effect on COD Reduction | 68 |
| 3.2.1.3 | Effect of Reaction Time on COD Reduction | 70 |
| 3.2.1.4 | Using Catholyte as a Coagulant Aid | 70 |
| 3.2.1.5 | Use of Anolyte and Catholyte in Jar Test | 72 |
| 3.2.1.6 | Biodegradability of Passivation Waste after Treatment with Anolyte and Catholyte Using GC-MS and IR Spectroscopy | 73 |
| 3.2.2 | Results and Discussion | 76 |
| 3.2.2.1 | Characteristics of the Passivation Waste | 76 |
| 3.2.2.2 | Anolyte and Catholyte Effect on COD Reduction | 76 |
| 3.2.2.3 | Effect of Reaction Time on COD Reduction | 83 |
| 3.2.2.4 | Using Catholyte as a Coagulant Aid | 85 |
| 3.2.2.5 | Use of Anolyte and Catholyte in Jar Test | 89 |
| 3.2.2.6 | Biodegradability of Passivation Waste after Treatment with Anolyte and Catholyte Using GC-MS and IR Spectroscopy | 90 |
| 3.2.3 | Summary | 118 |
| 3.3 | Activated Solutions in Treating Landfill Leachate | 119 |
| 3.3.1 | Experimental Studies | 119 |
| 3.3.1.1 | Characteristics of Leachate | 119 |
| 3.3.1.2 | Activated Solutions for Treating Leachate | 120 |
| 3.3.1.3 | Biodegradability of Passivation Waste after Treatment with Anolyte and Catholyte Using GC-MS and IR Spectroscopy | 121 |
| 3.3.2 | Results and Discussion | 124 |
| 3.3.2.1 | Characteristics of Leachate | 124 |
| 3.3.2.2 | Activated Solutions for Treating Leachate | 124 |
| 3.3.2.3 | Biodegradability of Passivation Waste after Treatment with Anolyte and Catholyte Using GC-MS and IR Spectroscopy | 126 |
| 3.3.3 | Summary | 132 |



| | | |
|-------|---|-----|
| 4 | CASE STUDY | 133 |
| 4.1 | Materials and Methods | 134 |
| 4.2 | Results and Discussion | 138 |
| 4.2.1 | Physical Treatment (with Rubberizer®) | 138 |
| 4.2.2 | Chemical Treatment (with ECA solution) | 139 |
| 4.2.3 | Biological Treatment (with anaerobic process) | 143 |
| 4.2.4 | Biological Treatment (with aerobic process) | 144 |
| 4.2.5 | Physical Treatment (with sedimentation) | 145 |
| 4.3 | Summary | 145 |
| 5 | CONCLUSION AND RECOMMENDATION | 146 |
| 5.1 | Conclusion | 146 |
| 5.1.1 | Study on the Characteristics of the Activated Solutions Generated | 146 |
| 5.1.2 | Activated Solutions In Treating Passivation Waste | 146 |
| 5.1.3 | Activated Solutions in Treating Landfill Leachate | 147 |
| 5.1.4 | Case Study | 148 |
| 5.2 | Recommendation for Further Studies | 148 |
| | REFERENCES | 149 |
| | APPENDICES | 161 |
| | VITA | 195 |



LIST OF TABLES

| Table | Page |
|--|-------------|
| 1.1 : Characteristics of the STEL@-ECA unit system | 6 |
| 1.2 : Some chemical reactions possible under electrochemical treatment | 9 |
| 1.3 : Reactive ions and free radicals formed in the anolyte and catholyte solutions by ECA | 10 |
| 1.4 : Specifications of anolyte and catholyte solutions | 11 |
| 2.1 : The evolution of technical ECA system | 21 |
| 2.2 : Duration of temporary disability period on the ways of treatment | 31 |
| 2.3 : Percentage reduction of microflora after using ECA solution | 32 |
| 2.4 : Filonenko's experiments findings for sanitary treatment of equipments in the poultry meat processing shops | 35 |
| 3.1 : Change of pH in anolyte and catholyte at different saline pump speed | 54 |
| 3.2 : IR spectral data for anolyte | 60 |
| 3.3 : IR spectral data for catholyte | 60 |
| 3.4 : The metal ions present in catholyte | 61 |
| 3.5 : Rate constants for the decomposition of Cl_2 , ClO_2 , Cl^- , O_2 and O_3 | 66 |
| 3.6 : Methods to characterize passivation waste | 67 |
| 3.7 : Dosage I for passivation waste | 68 |
| 3.8 : Dosage II and III for passivation waste | 69 |
| 3.9 : Dosage for testing catholyte as a coagulant aid using different catholyte concentration | 70 |
| 3.10 : Dosage for testing catholyte as a coagulant aid using different alum, catholyte and polymer concentration. | 71 |
| 3.11 : The methods used for GC-MS analyses for passivation waste | 75 |



| | |
|--|------------|
| 3.12 : Characteristics of the passivation waste | 76 |
| 3.13 : Coagulation and flocculation with catholyte using different catholyte concentration | 85 |
| 3.14 : Coagulation and flocculation with catholyte using different alum, catholyte and polymer concentration | 86 |
| 3.15 : Jar test results | 89 |
| 3.16 : Percentage reduction in COD and ferum after Stage I and II | 89 |
| 3.17 : Compounds Identification for Sample I, II, III of passivation waste | 95 |
| 3.18 : Percentage reduction of compounds in Sample II and III | 97 |
| 3.19 : Transformation Data for Sample II and III | 98 |
| 3.20 : IR Spectral results for Sample I | 114 |
| 3.21 : IR Spectral results for Sample I | 115 |
| 3.22 : IR Spectral results for Sample III | 116 |
| 3.23 : Methods used to analyze the characteristics of leachate | 119 |
| 3.24 : Dosage of anolyte and catholyte for treating leachate | 120 |
| 3.25: The methods used for GC-MS analyses of landfill leachate | 123 |
| 3.26 : The characteristics of leachate | 124 |
| 3.27 : pH, COD, ammoniacal nitrogen, turbidity and metal reduction after treatment with anolyte and catholyte | 124 |
| 3.28 : Compounds identification for Sample I, Sample II and Sample III of leachate. | 130 |
| 4.1 : Characteristics of the chemical wastewater | 133 |
| 4.2 : Description of the 6 points monitored of the treatment system | 135 |
| 4.3: Data collection on day 8, 28, 34, 84, 87,112, 119 and 135 for case study | 140 |

LIST OF FIGURES

| Figure | Page |
|---|------|
| 1.1 : Flow-through Electrochemical Modular, FEM | 3 |
| 1.2 : Generation of anolyte and catholyte in a diaphragm-type-flow-through electrochemical modular | 8 |
| 2.1 : The efficiency of bacteria number reduction in the septic dressing-room air depending on the ways of treatment. | 29 |
| 2.2 : The effectiveness of the electrolysis system in reducing BOD and COD | 42 |
| 2.3 : Dose response of <i>Legionella pneumophila</i> on different types of oxidants | 43 |
| 3.1 : Set-up of the STEL® system | 47 |
| 3.2 : Graph of concentration of chlorine versus saline pump flow | 52 |
| 3.3 : Graph of pH of anolyte versus saline pump flow | 53 |
| 3.4 : Graph of pH of catholyte versus saline pump flow | 53 |
| 3.5 : Graph of flow rate of anolyte versus saline pump flow | 55 |
| 3.6 : Bar graph of ratio of anolyte/catholyte versus saline pump flow | 55 |
| 3.7 : IR spectrum of anolyte | 58 |
| 3.8 : IR spectrum of catholyte | 59 |
| 3.9 : Graph of concentration of chlorine versus time | 62 |
| 3.10 : Graph of ln concentration of chlorine versus time | 62 |
| 3.11 : Graph of concentration of chloride versus time | 63 |
| 3.12: Graph of concentration of oxygen versus time | 63 |
| 3.13 : Graph of concentration of chlorine dioxide versus time | 64 |
| 3.14 : Graph of concentration of ozone versus time | 64 |

| | |
|---|------------|
| 3.15 : Graph of COD versus anolyte added | 77 |
| 3.16 : Graph of turbidity versus anolyte added | 77 |
| 3.17 : Graph of pH versus anolyte added | 78 |
| 3.18 : Graph of COD versus catholyte added | 78 |
| 3.19 : Graph of turbidity versus catholyte added | 79 |
| 3.20 : Graph of pH versus catholyte added | 79 |
| 3.21 : Graph of COD versus anolyte and catholyte added | 80 |
| 3.22 : Graph of turbidity versus anolyte and catholyte added | 80 |
| 3.23 : Graph of pH versus anolyte and catholyte added | 81 |
| 3.24 : Graph of COD (passivation waste) versus anolyte contact time | 83 |
| 3.25 : GC-MS spectrum for Sample I (original passivation waste) | 92 |
| 3.26 : GC-MS spectrum for Sample II (original passivation waste after treatment with anolyte) | 93 |
| 3.27 : GC-MS spectrum for Sample III (original passivation waste after treatment with catholyte) | 94 |
| 3.28 : Transformation of 3-methyl-p-anisaldehyde to hexane using catholyte | 100 |
| 3.29 : Transformation of methylphenidate acetate to 1-(2-methyl-1-propenyl)-piperidine using catholyte | 101 |
| 3.30 : Transformation of 2,4,6-trimethyl-pyridine hexane using catholyte | 102 |
| 3.31 : Transformation of 2,4,6-trimethyl-pyridine to propane using catholyte | 103 |
| 3.32 : Transformation of 3-ethyl-2-hydroxy-2-cyclopenten-1-one to 2-acetylcyclopentanone and 3-methyl-1,2, using catholyte | 104 |
| 3.33 : Transformation of 1,3-benzenedicarboxylic acid to hexyl vanillate using catholyte | 105 |



| | |
|--|-----|
| 3.34 : Transformation of 3-methyl-p-anisaldehyde to carbon dioxide and water using anolyte | 106 |
| 3.35 : Transformation of 1,3,4-trimethyl-6-cyclohexylbenzene to hexane using catholyte | 107 |
| 3.36 : Transformation of 4-(methylthio)-benzoic acid to hexyl vanillate using catholyte | 108 |
| 3.37 : Transformation of 2,4,6-trimethyl-pyridine to carbon dioxide and water using anolyte | 109 |
| 3.38 : Pathway showing how 1-pentadecene is produced using catholyte | 110 |
| 3.39 : Transformation of 1,3-benzenedicarboxylic acid to carbon dioxide and water using anolyte | 111 |
| 3.40 : Transformation of 1,3,4-trimethyl-6-cyclohexylbenzene to hexane, carbon dioxide and water using anolyte | 112 |
| 3.41 : IR spectrum for Sample I (original passivation waste) | 117 |
| 3.42 : IR spectrum for Sample II (original passivation waste with anolyte) | 117 |
| 3.43 : IR spectrum for Sample III (original passivation waste with catholyte) | 118 |
| 3.44 : GC-MS spectrum for Sample I (leachate) | 127 |
| 3.45 : GC-MS spectrum for Sample I (leachate) | 128 |
| 3.46 : GC-MS spectrum for Sample I (leachate) | 129 |
| 4.1 : Schematic diagram of the system configuration of the reactor (case study) | 136 |
| 4.2 : Monitoring the six points of the system (case study) | 137 |
| 4.3 : Percentage removal of COD using Rubberizer® | 139 |
| 4.4 : Percentage removal of COD using anolyte | 142 |
| 4.5 : Percentage removal of COD using anaerobic treatment | 143 |
| 4.6 : Percentage removal of COD using aerobic treatment | 144 |
| 4.7 : Percentage removal of COD with sedimentation | 145 |



LIST OF ABBREVIATIONS

| | |
|---------|---|
| ECA | Electrochemical Activation Process |
| FEM | Flow-through Electrochemical Modular |
| THM | Trihalomethanes |
| CIS | Commonwealth of Independent States |
| VAC | Voltage Alternating Current |
| PTFE | Polytetrafluoroethylene |
| COD | Chemical Oxygen Demand |
| BOD | Biochemical Oxygen Demand |
| UV | Ultraviolet |
| EAW | Electroactivated Water |
| GC-MS | Gas-Chromatography-Mass Spectroscopy |
| ICP-AES | Inductively Coupled Plasma-Atomic Emission Spectroscopy |
| FTIR | Fourier Transform Infrared |
| TLC | Thin Layer Chromatography |
| min. | minutes |



CHAPTER 1

INTRODUCTION

1.1 General

Coping with the improving world today i.e. industrial development, obtaining clean and hygienic water has gradually become a major concern to the entire human race. To overcome this problem, many scientists from all over the world have carried out studies and research on water and wastewater treatment. However, these serious problems did not stop. In fact, more 'water' problems were encountered. As mankind begin to develop the awareness of the importance of water, their assessments towards the value of water will be increased. One of the earliest attempt of mankind being involved in water treatment was in the nineteenth century¹. Their efforts of using chlorine as a disinfectant to fight waterborne human diseases such as cholera and typhoid were a successful one². Since then, water disinfection has created interests in mankind.

For several decades, chlorine, in different forms, has always played the role as a dominant disinfectant³. However, as mankind's concern on the protection of public health grows stronger, more and more questions on whether chlorination could bring a long-term, side effect to human health are often raised. This is because chlorine forms halogenated by-products, which are believed to have mutagenic and carcinogenic properties⁴. A good disinfectant must be toxic to microorganisms at concentrations well

below the toxic thresholds to humans and higher animals⁵. This is true, but in order to produce an alternative disinfectant which is effective and able to fulfill the above requirements is not an easy task. Alternative disinfectants such as ozone and UV radiation have been used but due to their high operation costs and non-residual effect (do not provide long-term protection), the ideal disinfectant is yet to be found.

1.2 Electrochemical Activation (ECA)

ECA is a well-known Russian technology introduced by a Russian scientist, V.M. Bakhir in 1972. Essentially, ECA concept involves the passage of a high frequency, high voltage current through a saline solution, with a membrane interposed between the anode and cathode and resulting in a substantial electrical potential difference which leads to the formation of two types of water, namely the 'anolyte' and 'catholyte'^{6,7}. The anolyte, often known as 'activated water' or 'oxidized water', is a mixture of reactive species, which contributes to special oxidizing, sterilizing and disinfecting properties of the anolyte. Despite its powerful properties, anolyte is non-toxic and harmless, both to human and the environment for it is biodegradable after some 48 hours⁸. This is because the small concentrations of free chlorine in anolyte and its low redox potential do not favor the formation of toxic trihalomethanes (THM) or other halogenated by-products⁹. STEL®, a device system designed for generation of aqueous ECA solutions specially for washing, disinfectant and sterilizing was launched in 1990 under the supervision of V.M. Bakhir, Ph.D. and Yu.G. Zadorozhny¹⁰. Today, thousands of the STEL® devices meant for producing electrochemically activated solutions operate in different cities of Russia

and CIS countries¹¹. These devices are widely used in clinical and medical preventive facilities, municipal economy institutions, health spas and swimming pools¹². ECA research is strongly supported by the government of the Russian Federation.

1.3 Flow-through Electrochemical Modular (FEM)

The key difference between new ECA technology and traditional electrochemical processes is the incorporation of a special flow-through diaphragm-type electrochemical reactor, called FEM. The new flow-through electrolytic modular elements has no analogues in the world¹¹ (Figure 1.1).

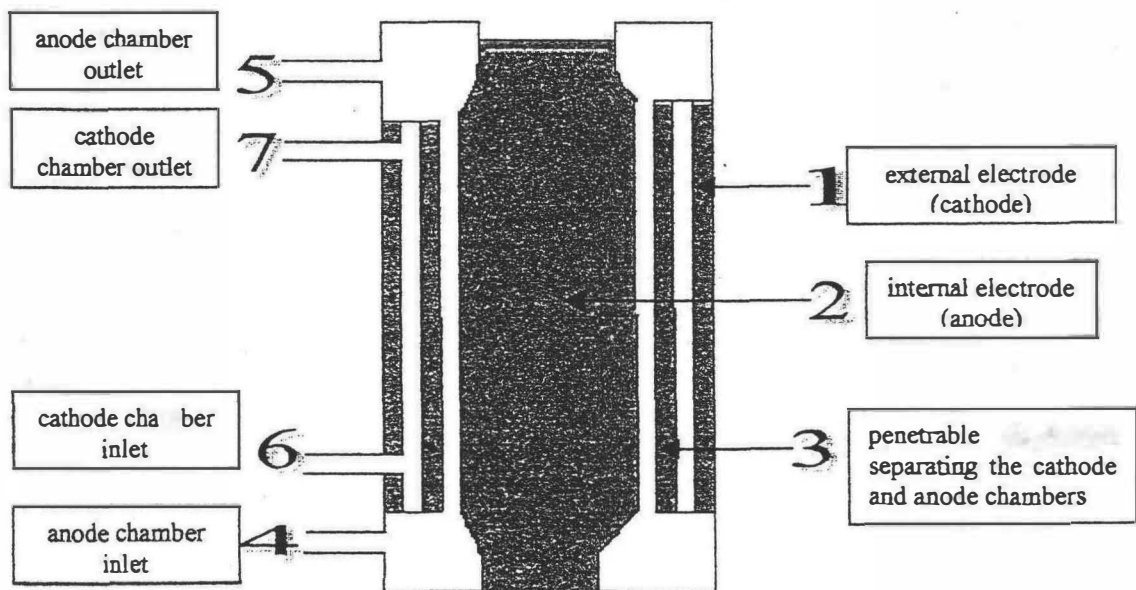


Figure 1.1: Flow-through Electrochemical Modular, FEM¹³

The electrochemical module makes use of two insulated rhodium plated, titanium electrodes where the two electrodes are separated by a patented zirconium oxide diaphragm¹⁴. The advantage of using FEM elements fitted in the electrochemical system is the generation of electrochemically activated, metastable solutions from low-mineralized initial solutions or natural water. This includes the anolyte, produced from the STEL® ECA system, which contains a mixture of hydrogen peroxide, chlorine dioxide, ozone, sodium hypochlorite, oxygen and other highly reactive species. The concept and theoretical aspects of this new technology in the field of applied electrochemistry was not fully and clearly discussed in any of the references obtained on this subject. The ECA technology is a sole Russian invention where all experts and specialists in this field are citizens of the former Soviet Union¹¹. According to Bakhir⁹, the design of FEM-3 elements (the third generation of the FEM invention) ensures the contact of all microvolumes of water flowing through the anode or cathode electrode chamber with an electrode surface, in the vicinity of which (in so-called Double Electric Layer, DEL) the electric intensity reaches few millions volts per centimeter (the effect of purification of rainwater and its saturation with vital power during spring thunderstorms). In this case, the processes of natural oxidation-reduction destruction and neutralization of toxic substances are accelerated both due to direct electrochemical reactions and as a result, highly active components electrochemically synthesized out of the water under treatment, such as ozone, atomic oxygen, peroxide compounds, active chlorine compounds, including chlorine dioxide, and short-lived free radicals.

1.4 The STEL® ECA System

1.4.1 Space Age Technology

The STEL® ECA technology was developed and patented as part of a Space Age StarWars Program over a period of 20 years at a cost of about US\$20 million for the treatment and recycling of water¹⁵. This is because in the space program, the astronauts have a limited amount of water which they can take with them and in turn has to be continuously purified and recycled for long missions and long term orbital stays. Therefore, the ECA based water purification systems was invented and successfully supplied water to keep the astronauts in space for even up to a year.

1.4.2 Characteristics of the STEL® ECA System

The STEL® ECA system is a device system designed to generate anolyte and catholyte using the ECA process. The characteristics of the STEL® ECA system are shown in Table 1.1.