

## GUIDELINES FOR THE PREPARATION OF WHITE PAPER

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**Geoenvironmental Research Experience** (list projects in progress or completed within the past 5 years):

Erie Pier Project, Duluth MN (Wittle and Doering)  
New Jersey Pesticide Site (Doering)  
Georgia Site (Doering)  
Montana Site (Wittle)

**Geoenvironmental Teaching Experience** (list related courses, including short courses, taught within the past 5 years):

**Geoenvironmental Consulting Experience** (list major projects onl  
**Appraisal of Geoenvironmental Research, Education and Practice** (limit to 1-2 pages):

## Curriculum Vitae

### Personal Data

Name: Dr. Falk R. Doering

Residence: 51, Burghaldenweg, Stuttgart, D-70469, Germany

Date/Place of Birth: June 19, 1941 in Dresden (Germany)

Marital Status: Married, two children (1968, 1971)

Languages: German, English, French, Russian

Member in Professional Organizations: Union of German Engineers (VDI), Union of Engineers for Soil and Groundwater Remediation (ITVA); International Electrochemical Soil Remediation Network

### Training

May 1961 to June 1995 University of Marburg; Geophysics and Business Administration

June 1995: MA in Geophysics; MBA  
August 1968: PhD

October 1968 to June 1973 University of Bonn, law and International Private Law  
June 1971: LL.B

### Professional Career

Dec. 2000 to ... electrochemical processes, I.I.c. (ecp), Valley Forge (PA), CEO and Owner. ecp is the controlling holding of different affiliate companies such as: P2 Soil Remediation, Inc., Stuttgart (Germany), Eurodépollution s.à.r.l., Irigny (Greater Lyon), France, B.S. Geoteknik ApS, Odense (Denmark), BUGS s.à.r.l., Niederkorn (Luxemburg):

- worldwide geophysical exploration of raw materials such as petroleum, natural gas, gold, uranium, diamonds, and rare metals
- performance of projects of soil and groundwater remediation with own technologies (engineers and general contractors)
- R&D in electrochemical processes for land remediation and commercial application of these processes as general contractor in the brownfield development
- R&D in waste water treatment and saline water conversion by RO, UF, UV, UHF-radiation.

## **J. KENNETH WITTLE, PH.D.**

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### **Education:**

Business Administration	1970	The Wharton School
Ph.D. Chemistry	1968	Purdue University
B.A. College	1962	Franklin & Marshall

General Electric Continuing Education Program: Management Development Course, Modern Engineering

### **Work Experience:**

#### **9/1979 – present**

Vice President, Electro-Petroleum, Inc.

Electro-Petroleum, Inc. developed a process with the utilization of electrical energy to stimulate oil production in heavy oil formations. The process demonstrated a 300% increase in oil production of electrically stimulated wells. This process is now being applied to soil remediation and site cleanup in the environmental field.

#### **1/1984 – present**

Vice President, Electro-Pyrolysis, Inc.

Electro-Pyrolysis, Inc. holds the patents (co inventor) for a DC arc furnace process for the destruction of hazardous and municipal solid waste by ultrahigh temperature pyrolysis.

#### **2003 - present**

Developer and operator of Coleraine, MN Research Sediments Testing Facility

#### **1996 - 1997**

Adjunct Professor for Environmental Engineering, Clemson University, Clemson, SC

#### **1992 - 1994**

Visiting Scientist, Massachusetts Institute of Technology, Plasma Fusion Center, Cambridge, MA

#### **1985 – 1990**

Cofounder of TTW, a company formed to develop deep drilling equipment for the oil and gas industry

#### **1985 – 1992**

Co founded ITA, technical consultants to a private investment capital group

#### **1/1979 – 1987**

Consultant, Planning and Siting, ChemClear, Inc.

Responsible for planning and siting work for a public access company in the liquid industrial aqueous waste treatment business. Patented a process for electrically drying of aqueous sludges.

#### **1968 – 1979**

## General Electric Company

1972 – 1979 Dielectric Materials Laboratory Manager

- Directed development and testing of organic and inorganic material used in design and manufacturing of low, medium, and high voltage switchgear, high voltage transformers, and relays. Included electrical, mechanical, and chemical testing laboratories.

1968 – 1972 Sr. Inorganic Chemist, Sr. Project Engineer

### **1972 – 1979**

Dielectric Materials Laboratory Manager

Directed development and testing of organic and inorganic material used in design and manufacturing of low, medium, and high voltage switchgear, high voltage transformers, and relays. Included electrical, mechanical, and chemical testing laboratories.

### **1968 – 1972**

Sr. Inorganic Chemist, Sr. Project Engineer

### **Publications:**

50 technical papers and 30 + U.S. and foreign patents

### **Technical Societies:**

Dr. Wittle is a member of the American Chemical Society, The Chemical Society, American Association Advancement of Science, Society of Petroleum Engineers, and American Society of Mechanical Engineers. Dr. Wittle is Chair of the ASME Research Committee on Industrial and Municipal Waste and Vice Chair for the Board on Research of the Board on Research and Technology Development. Dr. Wittle served as a member of the Diffusion Focus Group of the Technology Innovation and Economic Committee of NACEPT (National Advisory Council for Environmental Policy and Technology) and advisory committee to the U.S. Environmental Protection Agency.

### **Perspective on Emerging Geoenvironmental Issues and Technologies (limit to 1-2 pages):**

#### **Basics of ElectroChemical GeoOxidation (ECGO)**

Dipl.-Ing. Niels Doering P.E., Dr. Falk Doering, VDI, ecp, llc., Wayne (PA)

#### Rationale

For more than a century, electrochemistry is an essential branch of the chemical industry. Electrochemical processes are subdivided in (a) the Electrochemical Synthesis, covering a wide field of applications ranging from the synthesis of organic substances, resins, artificial materials, cellulose, inorganic chemicals (chlorine, oxygen, hydrogen), and semiconductors, and serves the sterilization of sera. (b) Electrokinetic Processes make fuel cells and batteries work; basic applications are electrochemical machining, electro-forming, etching of metals, etching of semiconductors, liquid/solid separation, electroplating, electrophoretic painting; whereas (c) Joule heating (resistance heating) is used for smelting metals such as steel and aluminum, and to produce artificial crystals such as diamonds or zirconium. Modern technologies such as lasers and plasma based processes are unthinkable without electrochemical foundations. There is no logic reason, to see on the one hand these processes in laboratories and factories work, and on the other to contest the viability of the same processes when being implemented in soils and the groundwater.

With respect to synthesis and electrokinetics, ElectroChemical GeoOxidation (ECGO) transfers above technologies into the soil and the groundwater. Of course, the special conditions of the medium, the soil, need to be considered as process requirements. We should mention that in soils already natural electrical fields exist named "Spontaneous Polarization" (C. SCHLUMBERGER) which are in the range of 150 to 2,000 mVDC.<sup>1</sup> These natural voltages already perform electrochemical reactions (redox-reactions) in the soil and form integral part of "natural attenuation".

ECGO comprises a bundle of five different processes addressing special problems such as mineralization of organic compounds, treatment of sediments (humic substances), treatment of large surfaces (tank farms, refineries, manufactured gas plants), remediation of mixed damage (organic/inorganic pollutants) and metal-organic pollutants, and finally heavy metals. An ECGO system comprises of - at least - two steel electrodes incorporated into the soil. Via these electrodes a predefined electric dc-current is introduced into the soil effecting redox-reactions which mineralizes organic pollutants to carbon dioxide and water. System variants are designed to have heavy metal ions and complex ions precipitate onto the electrodes. ECGO can be applied in multi-electrode systems. The length of the electrodes is commensurate to the depth of the damage; the distance between the electrodes is between 5 m to 300 m, dependent on the type of ECGO process to be applied.

Hereinafter, we discuss the essential elements of ECGO, namely the double (triple) layer structure related to the soil particle/electrolyte system, Induced Polarization, and the system of redox-reactions (reduction/oxidation reactions).

#### The Double (Triple) Layer Structure

Civil Engineering Sciences and hydrogeology very early started investigations into the soil/groundwater system defining groundwater as electrolyte. In the following, also the pollutants distributed in the soil, are referred to as "soil particle". To be mentioned first, two approaches to the electrochemical description of the soil are used. Some European scientists (SCHAAD, JORDAN, DOERING et al.) prefer the microscopic approach comprising of the "Colloid Model" and the double (triple) layer water hulls, bound by electrostatic forces to the soil particles whereas the majority of US scientists (VACQUIER, MADDEN, MAYPER, CANTWELL et al.) prefers the macroscopic approach comprising of the concept of the cation-selective membranes.

The Colloid Model is based on the research of ETH Zurich<sup>2</sup> that any soil particle, once being in contact with the soil water (commonly referred to as groundwater), builds up a double layer with the water. Driving force of this phenomenon are so-called electrostatic forces such as VAN-DER-WAAL, LONDON, COULOMB etc. forces creating the so-called adsorption-complex comprising of the highly viscous, highly pressurized (pore water pressure  $p_w = 10,000$  to  $25,000$  bars) hygroscopic water hull, and the so-called solvation water layer, attracted by the residual electrostatic forces, having a lower viscosity. The third layer is called captive water, marking the transition area to the bulk solution (groundwater) with very little electrostatic forces. The electrical charge in the soil particle/electrolyte system is determined according to COEHN's law: the substance or particle having the higher dielectric constant, obtains the positive charge. As a rule, water having a dielectric constant  $\epsilon \geq 80$  (at about 20°C) is almost in all cases positively charged.<sup>3</sup> Thus, the double layer in reality is a triple layer structure which works as capacitor. The capacity of the soil is in the range of about 5 to 50  $\mu\text{F}$  may substantially increase over time by the phenomenon of the electrostriction, i.e. the contraction of the dielectric layer attributable to the attraction of the dipoles which is:

$$DV / V \sim \epsilon E^2$$

where:  $\Delta V / V$  = the rate of contraction

$\epsilon$  = permittivity

E = voltage applied.

The individual capacitors linked with the corresponding resistors in the soil form RC-elements which are the key element of energy supply to the redox-reactions. This terminology taken from hydrogeology may now be made compatible with the terminology of the colloid chemistry. The above mentioned

hygroscopic water corresponds to the Inner Helmholtz layer; the solvation water to the term “Outer Helmholtz Layer” and the captive water is the “Diffuse Layer”. Between the Outer Helmholtz Layer and the diffuse layer, there is an interface, called Outer Helmholtz Plane, the prerequisite for electrochemical reactions, where the transfer of electrons takes place. The voltage gradient between the interface and the bulk solution (groundwater) is known as Zeta-potential.

Explaining Induced Polarization in a macroscopic approach, VACQUIER et al. described in 1957 a model wherein an electrical field drives cations and water through a cation-selective membrane (= capillary system of the soil), whereas the anions are rejected by the Helmholtz double layer of the capillaries.<sup>4</sup> This model could not, however, be confirmed in the field since both, anions and cations, are driven through the capillaries.

### Induced Polarization

In soils already natural electric dc fields exist (“Spontaneous Polarization”, SP). The process of upgrading the voltage of SP is commonly referred to as Induced Polarization (IP), a geophysical phenomenon subject to intensive research in the U.S. in the fifties and sixties of the past century. IP explains the effects of an electrical current passing through the soil. Two different phenomena have been detected: when the particles of the soil are conductive, then on the so-called faradic path redox-reactions occur, i.e. when electrons cross the interface (Outer Helmholtz plane), electrochemical reactions and ion diffusion take place. These processes can easily be identified by oscilloscope as impedance of the system, subdivided into the reaction-impedance, and the Warburg impedance (characterizing the ion diffusion). Algorithms have been developed to calculate either share at the impedance. When the particles of the soil, however, are insulators, then on the non-faradic path electrons are stored in the triple layer. The discharge signals can be identified in the oscillograms as spikes. The capacitance of the soil increases over time and is the major supplier of energy to the reactions, in particular, for overcoming the activation energy.<sup>5</sup>

### The Soil as Conductor

Traditional geophysics describe two different types of conductors in soils, namely the ionic conductor, comprising of the groundwater containing ions, and the electronic conductor, in most cases metallic minerals or minerals doped with metals. Metallic minerals are alloys, minerals such as  $Mg_2Pb$ ,  $Mg_3Sb_2$ ,  $Fe_3O_4$  (magnetite) and graphite, whereas other minerals such as  $CaCO_3$ ,  $Sb_2O_3$ , Hematite ( $\alpha-Fe_2O_3$ ), or  $HgS$  are insulators. The conductivity of the so-called metallic (electronic) conductors apparently depends on the position of the metal atoms in the crystal lattices. Since the majority of minerals, despite the inclusion of metal atoms, has resistivities between  $10^6$  and  $10^{15} \Omega m$ , this type of conductor can only be considered to be representative for certain ore deposits. In regular soils, the electronic conductor is of marginal importance.<sup>6</sup>

It is a basic understanding in geophysics that the resistivity of the soil largely depends on its water content.<sup>7</sup> The conductivity of the groundwater (fresh water) is in the range of  $250 \mu S / [25C^\circ]$  to about  $700 \mu S/cm$  which corresponds to about  $40 \Omega m$  to  $14.3 \Omega m$ . This conductor is called the Ionic Conductor.

In our field research, a third conductor has been discovered, namely the colloid conductor apparently using the Outer Helmholtz layer (dielectric layer) as conductor. This conductor has an extremely low resistance of 0.1 to about  $10 \Omega$  between two electrodes placed at a distance of 5 m to 100 m. This conductor has been called the Colloid Conductor on which electrons are forced to cross the interfaces thereby initiating reactions of oxidation and reduction. The resistance of this conductor is variable since field observations tend to indicate that its thickness fades out during remedial action. The colloid conductor is of primordial importance for ECGO, since it permits to drive a relatively high amperage at relatively low voltages. However, limitations are given by the microscopic size of the conductor. From a certain point onward, which is called the Electrokinetic Point (EP), the ionic conductor (the capillary water) becomes the main conductor permitting to drive high amperages at high voltages at an elevated resistance. The conductor is important for the distinction of electrochemical processes in the soil: the

colloid conductor is linked to electrochemical (redox-) reactions whereas the ionic conductor permits at substantially higher energy levels the transport of ions through the soil without electrochemical reactions.

### Redox-Reactions

Oxidation of organic substances stands for donation of electrons whereas reduction stands for acceptance of electrons. Both reactions occur simultaneously and require the presence of oxidizing and reducing agents. These agents are generated by ECGO in-situ by water electrolysis. By primary processes and secondary reactions, the agents are generated such as elemental  $H_{nasc}$ , HO radicals and ions,  $HO_2$  ions and radicals and hydroperoxide, as well as elemental oxygen ( $O_{nasc}$ ) and ozone.

Ongoing oxidation comprises of the generation of alcohols, aldehydes, organic acids which under the conditions of ongoing oxidation decompose to carbon dioxide and water where reduction means stepwise substitution of p.x. halogens by hydrogen, ring opening of aromatic constituents or cleavage of aliphatic compounds at preferred breaking points ( $C_{10/12}$ ;  $C_{5/6}$ ,  $C_{2/3}$ ).

In the literature, the application of Fenton's reagent, i.e. the synthesis of OH-ions and radicals from the in-situ reaction of hydroperoxides with bi-valent iron has been discussed. Since Fe is an ubiquitous mineral and since by water electrolysis, oxidants such as hydroperoxides are generated, the activity of Fenton's reagent cannot be excluded for ECGO.

The central objective of ECGO is to establish an oxidized environment at *pH* in the range of neutral and obtaining *Eh* (electrode potentials) in the range of the positive. This requirement in particular decides on the success or failure of the remediation of sediments which at *pH* in the range of 5.5 to about 8.5 have an *Eh* in the range of -250 mV to 200 mV (reducing, from 0 to -250 mV strongly reducing) whereas upland soils have a *pH* of about 5.5 to 8.5 and an *Eh* in the range of above 350 mV (above 500 mV: well oxidizing). Reduction would – as far as sediments are concerned – support “polymerization” processes of humic substances, using metal ions as “hook-up” points for the recombination of PAH-, phenol-, PCB- et al. molecules. First results of field tests related on the treatment of sweet water sediments indicate that ECGO can substantially raise the *Eh*. This result is still subject to confirmation<sup>8</sup>. In another test, dealing with sediments in the Baltic Sea, we intend to exploit the process of *Eh/pH* control to break up humic substances and to set TBT free which is expected to precipitate tin on the electrodes.

### A Field Research Project on the Decomposition of PAH

About 500 tons of a silty soil, polluted by 11,000 mg PAH<sub>EPA 1-16</sub> have been homogenized by sieving and then having been heaped. Because of the homogenization the average concentration of the heaped material decreased from 11,000 mg PAH/kg to 1,355 mg PAH/kg. In the heap, an anode and a cathode, were horizontally installed at a distance of 10 m, resulting in a resistance of 9.45 Ω. The remedial action took 70 days when the remedial action has been accepted by the regulator and 100 days when our quality control system stated the almost complete destruction of metabolites and by-products (TPH). The regulator relied on the sampling and the chemical analysis performed by an University, collecting composite samples and using method DIN 38407-F8 for the analysis of PAH by HPLC. The GC-MS chromatograms have been established on the basis of aliquots of the above samples by a hnu 321/Finnigan MAT ITD 800 system, using the NBS/EPA extended environmental library and the INCOS search system.

The clean-up levels were 100 mg/kg d.m. for PAH (EPA 1-16) and 15 mg/kg d.m. for 6 carcinogenic PAH, hereinafter referred to as PAH-TVO, namely Fluoranthene, Benzo(b)fluoranthene, Benzo(k)-fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)perylene and Ideno(1,2,3cd)pyrene.

The results prepared by the university, read as follows [mg/kg d.m.]:

<b>Days</b>	<b>1</b>	<b>36</b>	<b>70</b>
Naphtalene	80,7	81,3	17,29
Acenaphtylene	35,2	44,1	0,98

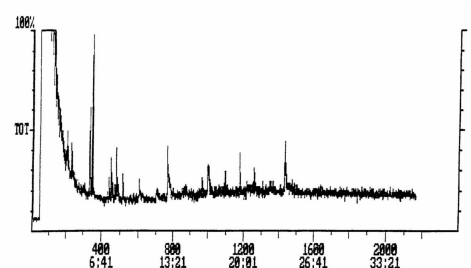
Acenaphthene	9,8	22,2	0,6
Fluorene	38,6	503,1	1,13
Phenanthrene	326,8	83,7	7,35
Anthracene	47,8	11,9	1,45
Fluoranthene	107,5	23,4	2,98
Pyrene	230,2	81	8,38
Benzo(a)anthracene	71,3	17,6	1,48
Chrysen	81,8	17,9	2,04
Benzo(b)fluoranthene	50,7	9,6	2,09
Benzo(k)fluoranthene	47,3	4,2	1,21
Benzo(a)pyrene	110,3	17,9	3,75
Indeno(123-cd)pyrene	47,8	26,2	1,09
Dibenz(ah)anthracene	9,5	25,6	2,98
Benzo(ghi)perylene	59,5	37,9	0,54
Total (1-16)	1354,8	1007,6	55,33
PAH TVO (6)	423,1	119,2	14,1

The decomposition (reduction by cleavage) is performed via 2-core (naphthalene) and 3-core PAH (here: fluorene, in other cases acenaphtylene).

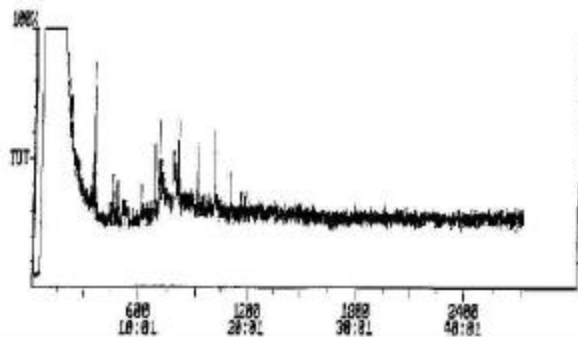
The GC-MS analysis was as follows whereby the by-products deserve special interest.

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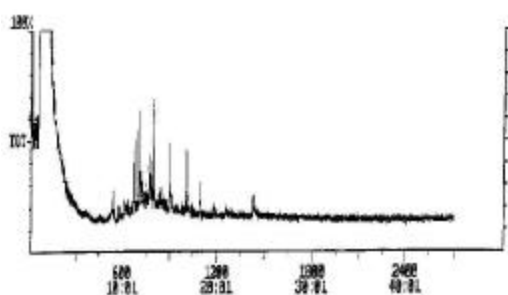
Baseline Sampling



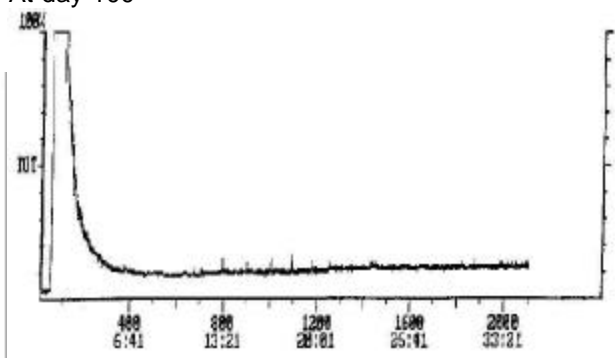
At day 36



At day 70 (official end of remedial action)



At day 100



During remedial action the basic pattern of the chromatograms changed: the baseline chromatogram is typical for a contamination by PAH, the chromatograms at day 36 and 70, however, are typical for TPH including the so-called "oil hill" (underground) which stands for a complex mixture of organic compounds dissolved in TPH. The chromatogram at day 100 depicts again close to the limits of detection a chromatogram typical for PAH. The statement can be made that the electrochemical decomposition of PAH is made

- a) by breaking up the molecules to levels of 2- and 3-core PAH and then ongoing
- b) breaking up the aromatic and cyclic compounds to aliphatic compounds (TPH)
- c) oxidation of the constituents to carbon dioxide and water.

At the end of the project, the metabolites have been eliminated to close to the limits of detection. Persistent metabolites could not be traced.

The following metabolites have been detected in the chromatograms of day 36 and 70: derivatives of benzene (butynylbenzene), and cyclic compounds (dodecyclomethyloxirane, 3-(1,1 dimethylethyl-cis cyclohexacarboxylic acid, cyclopentapyrane-1,3-dion) and 1,2,4-cyclopentanetron, 3-methyl).

In the final chromatogram (of day 100), 1,2,4 cyclopentanetron, 3-methyl, dimethylcyclohexane and propanoic acid, di-methyl-, have been identified.

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<sup>1</sup> J.S. Sumner: Principles of Induced Polarization for Geophysical Exploration; Elsevier Scientific Publishing Company, New York 1976; F. Ollendorff: Electric Current in Soils (in German), Birkhaeuser Verlag Basel, Stuttgart, 1969; Ch. Veder: The Importance of Natural Electric Fields for Electroosmosis and Electrokataphoresis in Soil Mechanics (in German) in: *Der Bauingenieur*, 38, (1963), p. 378

<sup>2</sup> W. Schaad: Practical Application of Electroosmosis in Soil Mechanics (in German) in: *Die Bautechnik*, 35 (1958), p. 210;

<sup>3</sup> T.M. Riddick: Control of Colloid Stability through Zeta Potential; Zeta Meter (ed.), Wynnewood, PA, 1968; H. Jordan, H.-J. Weder: Hydrogeology (in German), Leipzig (GDR), 1988; F.R. Doering and Th. Papadopoulos: In-situ Electrochemical Soil Remediation; Hazwaste World Superfund XVII, October 15-17, 1996, Washington, Conference Proceedings, p. 116

<sup>4</sup> V. Vacquier, C.R. Holmes et al: Prospecting for groundwater by Induced Polarization; *Geophysics*, 22, n° 3, 1957, p. 660

<sup>5</sup> D.F. Bleil: Induced Polarization; *Geophysics*, 18, n°3, 1953, pp. 636; D.J. Marshall, Th. Madden: Induced Polarization, A Study of its Causes; *Geophysics*, 24, 1959, p. 790 T.R. Madden, T. Cantwell: Induced Polarization: A Review. Mining Geophysics, Vol. II, ed.: Society of Exploration Geophysicists, 1967; J.W. Wait (ed.) Overvoltage Research and Geophysical Applications; Pergamon Press, London, New York pp., 1959, T.J. Katsube: The Electrical Polarization Mechanism Model for Moist Rock; *Geol. Survey of Canada*, paper 75-1C, p. 353; Grahame: Mathematical Theory of the Faradic Admittance; *Journal of the Electrochemical Society*, 99, 1952, p. 370C, only to mention a selection of papers

<sup>6</sup> D. Rahner, H. Gruenzig, G. Ludwig: A Study on the Electrochemical Remediation of Polluted Soils (in German, with reprints in English); Report of the Technical University of Dresden (Germany) to the EPA of Saxony, August 1995; see also: preceding publications by: A. Brandt: Geophysical Exploration, US.-Pat. 2 611 004 (1952), P. Mandel, J.W. Berg, K.L. Cook: Electrical Properties of Synthetic Metalliferous Ore; *Geophysics* 24, p. 510, I.I. Rokityansky. The Nature of Induced Polarization of Ion-Conducting Soils; Academy of Sciences of the USSR, Geophysical News, n°. 7, 1959, p. 752

<sup>7</sup> A.P. Krajev: Basics of Geoelectricity (in Russian), Moscow 1957

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<sup>8</sup> Patrick et al.: paper presented to the Workshop on: Environmental Stability of Chemicals in Sediments, San Diego  
April 8-10, 2003