A.10.5 La méthode des potentiels de jonction membranaires appliquée à l'évolution des isolants de cables.

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A.10.5 Membrane potential technique applied to the study of cable insulation modification

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Abstract :

This paper investigates the physico-chemical modifications of the insulating and the semi-conducting materials of electric cables.
Mineral impurities were detected by Neutron Activation Analysis in the dielectric material at the vicinity of the semi-conducting shields.
In order to study their migration from the semi-conductors to the insulating material, Membrane Potential Measurements were performed on slices of dielectric material of 40 µm thickness. The results obtained are characteristics of ion diffusion phenomenon.
Moreover, by the use of diagnostic techniques such as XPS, IR microscopy and contact angle measurements the presence of polar groups and in particularly carboxylic groups has been observed in the dielectric. These groups, acting as ionic carriers could foster the diffusion of mineral impurities to the dielectric bulk.

Résumé :

L'objectif de notre travail est d'étudier l'évolution physico-chimique des matériaux isolants et semi-conducteurs, des câbles électriques.
La présence d'impuretés minérales dans le diélectrique, au voisinage des écrans semi-conducteurs a été mise en évidence par Analyse par Activation Neutronique. Dans le but d'étudier la migration de ces impuretés du semi-conducteur vers le diélectrique, des mesures de Potentiel de Jonction Membranaire ont été effectuées sur des tranches de diélectrique de 40 µm d'épaisseur. Les résultats obtenus sont caractéristiques d'un phénomène de diffusion d'ions.
Par ailleurs, l'emploi de techniques d'analyse telles que l'XPS, la microscopie Infra-rouge et les mesures d'angles de contact a montré la présence dans le diélectrique de groupements polaires et en particulier de groupements carboxyliques. Ces groupements joueraient le rôle de transporteurs ioniques et favoriseraient la diffusion des impuretés minérales au coeur du diélectrique.

I- Introduction :

Over the last two decades a growing interest for the study of structural, electrical and dielectric behaviour of polyethylene has been developped for electrical insulation of high voltage power cables. The main results point out that the morphology, the additives and the impurities, oxidation and the thermal degradation, and traces of water play major roles in the ageing processes of polymers [1][2]. The cristallinity and the density of extruded insulations are affected by ageing and especially by prolonged exposition to elevated temperatures (80-100°C) [1]. Traces of oxidation were detected in aged insulations by FTIR and the carbonyl groups detected correspond to a decrease of the anti-oxidant level [1]. It appears that the semi-conductors loaded with furnace carbon black are a source of contamination since they contain many metallic and organic impurities [3]. Systematic studies have shown that metallic impurities migrate into the insulation [4][5] and initiate water or electrical trees [6][7].

The work described in this paper attempts to identify changes in the electrical properties of polyethylene aged cable insulation due to the presence of metallic impurities by new techniques such as membrane potential measurements and surface potential decay measurements. A correlation between these electrical properties and the physico-chemical modifications was established by using diagnostic techniques such as XPS, IR microscopy and contact angle image processing measurements.

II- Sample preparation of 63 kV cables dielectric material :

In order to evaluate cable ageing three 36/63 kV cables of the same manufacture (with an aluminum conductor of 260 mm^2 section and insulated with low density uncrosslinked polyethylene) were selected :

- a field aged cable (FA) manufactured in 1979 and took off after 11 years of service
- a new cable (N) manufactured the same year and stored up on a cable reel
- a cable subjected to a long duration test (AA : Artificially aged) ie aged for 6000 h at 63 kV and sumitted to 250 heating cycles with a maximum conductor temperature of 85°C [8]

For the scientific investigation we needed thin slices of material prepared by using a microtome specially modified for this purpose. According to the analysis techniques two thicknesses were chosen. 100 µm thick samples were used for XPS, contact angle measurements and surface potential measurements and 40 µm thick samples were used for membrane potential measurements.

III- Results and discussion :

III-1 *Identification of a mass transfer from the semi-conducting shields through an ageing dielectric material .*

In a first step Neutron Activation Analysis was performed in order to analyze mineral impurities in dielectric material and in the semi-conductor shields. In each type of the above mentioned cables five samples were taken away at different distances from the conductor (figure 1).

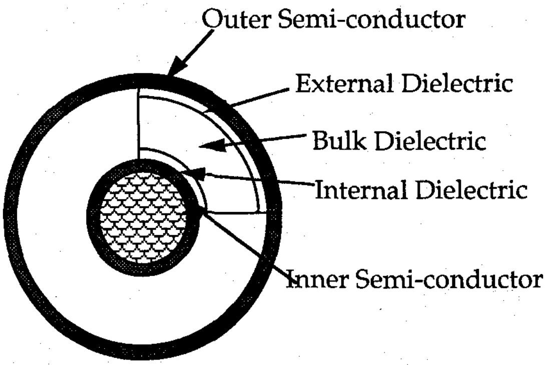

figure 1
Sampling for Neutron Activation Analysis

Generally, the impurity concentration is higher within the first mm of polyethylene adjacent to the semi-conducting shields and lower in the dielectric material bulk. The source of contamination appears to be the semi-conducting shields. The main elements detected are Zn, Br, Co, Cr, Na and Fe and the concentration profiles of Zn, Co , Br and Cr are presented on figure 2.

According to these results it is clearely noted that a diffusion mechanism of impurities occurs from the semi-conducting shields through the dielectric material. This phenomenon causes a concentration gradient of mineral elements in the polyethylene adjacent to semi-conductor/dielectric interfaces. It could be described as a mass transfer illustrating the transport properties of polyethylene used as insulating material.

III-2 *Demonstration of ionic carrier presence by membrane potential measurements in the dielectric material insulating cables*

In order to point out the dielectric ionic conductibility 40 µm thick slices of polyethylene were cut out of cables perpendicularly to the Z axis and introduced as a membrane in the experimental set up shown figure 3. The 40 µm thick sample is fixed with a Teflon tape at one end of an 8 cm long and 5 mm diameter pipe. For the validity of the measurements it is important to check that the membrane has not been damaged during the handling and that there is no leakage. The membrane potential measurements technique consists of measuring the evolution with the concentration of the potential difference between two solutions separated by the sample to be analyzed [9].

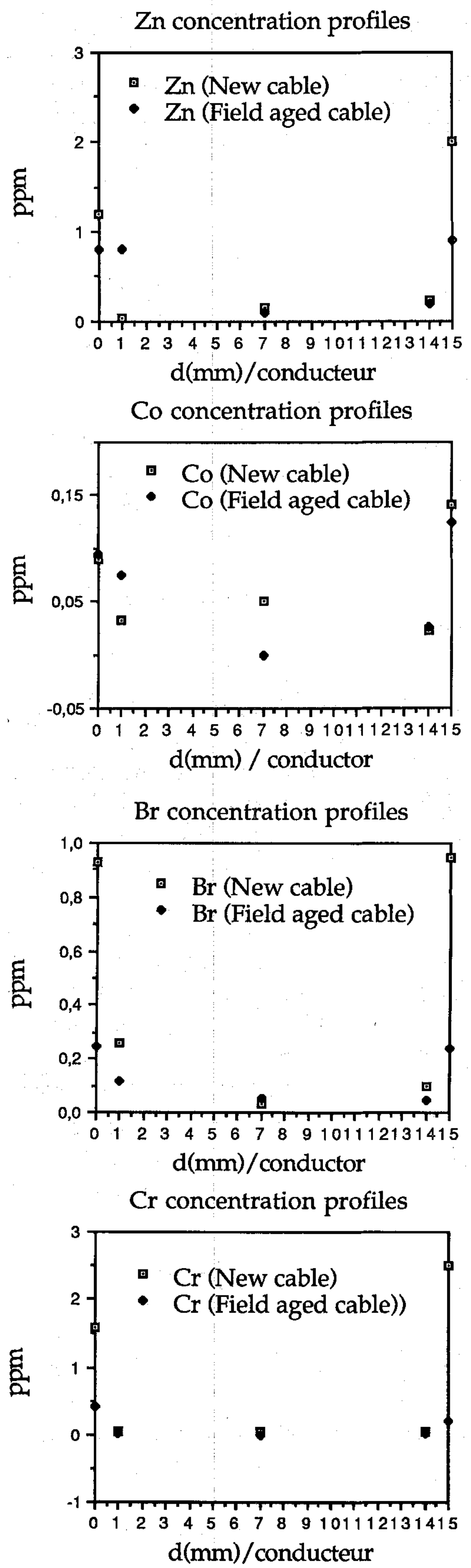

figure 2
Concentration profiles

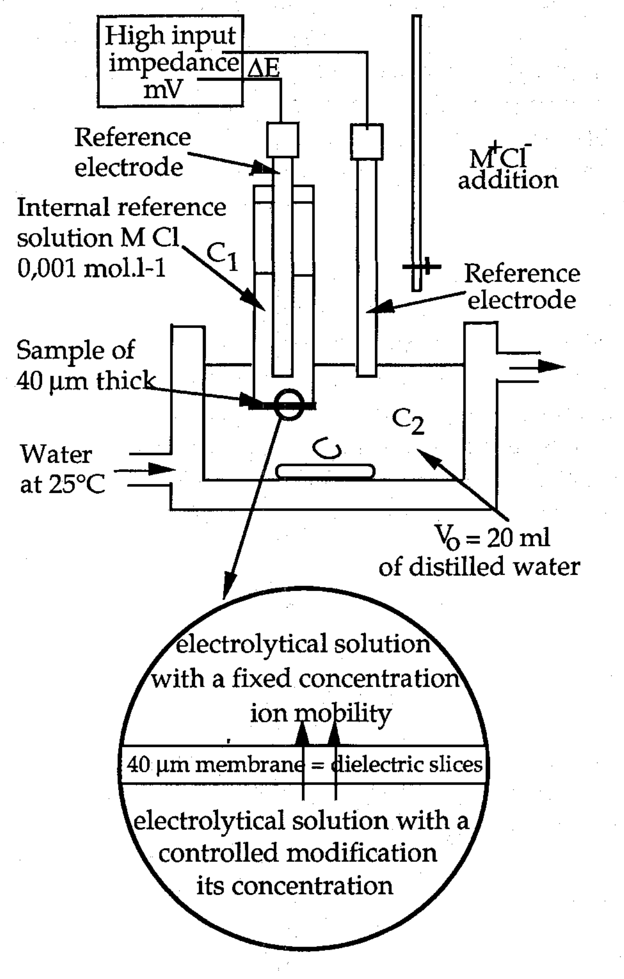

figure 3
Experimental set-up used for membrane potential measurements

Different salt solutions with proton or metallic cations were used. With a perfectly insulating membrane no measurement is possible. On the contrary, the existence of a potential difference ΔE point out an ionic conduction and involve the presence of ionic carriers . If this potential difference is compare to a diffusion potential, then ΔE can be written in the form :

$$\Delta E = k + (2t^+ - 1)\, RT/F \log C_1/C_2$$

with : k : constante including Nernst's parameters
t^+: cation transport number
C_1 : and C_2 concentrations (mol.l-1) of salts in each compartment

By this way it is possible to determine whether or not there is an ionic transport of cations such as H^+, K^+ and Na^+ through the polymer film [9][10]. Samples cut out of a new cable (N) appear perfectly insulating. For the artificially aged cable (AA) the sensitivity of the apparatus made measurements impossible. In both cases junction potential is very instable and no measurements is possible. Nevertheless these two types of samples have to be considered seperately. For the artificially aged cable absence of any response does not mean that there is no modification in the insulator. Indeed, measurements are made on the entire width of the insulator, whereas the ageing seems to begin at the dielectric/semi-conducting shield interfaces and to progress to the middle of the insulator. In the case of field aged cable (FA) the junction potential is stable and the accuracy of measurements is +/- 0,5 mV. The results obtained with HCl, KCl and NaCl (figure 4) point out transport properties.

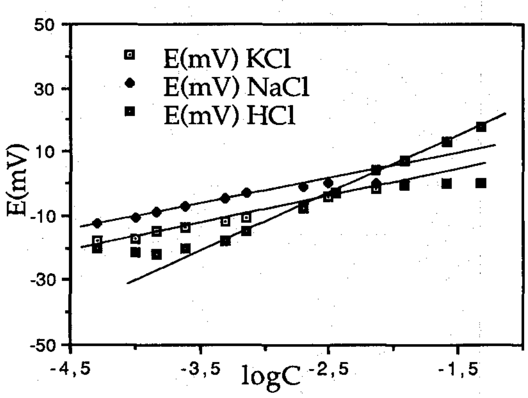

figure 4
Membrane potential results for field aged 40 µm thick polyethylene dielectric samples

The curves E(mV) versus logC are characteristic of cationic carriers presence ($t^+>0,5$) in the membrane. The slopes values indicate that $t^+_{H^+} >> t^+_{K^+} > t^+_{Na^+}$, then the selectivity of the material is higher for H^+ than for K^+ and Na^+. The transport numbers for H^+ , K^+ and $Na^+$are about : $t^+_{H^+}$=0,65 ; $t^+_{K^+}$=0,57 (E=8mV/log unit) ; $t^+_{Na^+}$=0,56 (E=7mV/log unit) .Thus, in the case of field aged cables (FA) , there is appearence of ionic conductibility which could be associated to the presence of ionic carriers. These carriers could stimulate the mineral impurities diffusion under electrical and temperature stresses.

By this new technique we pointed out the modification of the insulating material of the cable with ageing and in particularly the modification of its ionic transport properties. Nevertheless , correlation between ionic transport and electrical transport properties has to be demonstrated. Furthermore, we attempted to identify the physico-chemical changes in aged materials.

III-3 *Electrical surface conductibility of the dielectric material.*

In order to prove the modification of the dielectrical properties of the polyethylene used as insulating material in 63 kV cables, surface conductibility of 100 µm thick samples was studied. The method consists of exposing the sample to an injection of negative charges produced by a negative corona discharge; then the potential decay measured by an electrostatic probe is recorded in function of time. The scheme of the experimental set-up is presented figure 5.

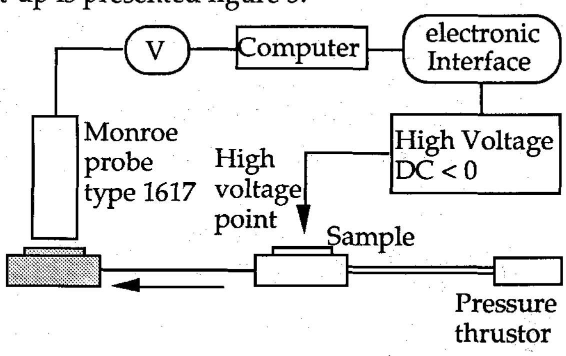

figure 5
Experimental set-up used for surface potential decay measurements

In the case of insulating material samples cut out of a new cable (N) no potential decay is observed. For field aged samples (FA), a more rapid dissipation of charges injected at the surface of the polymer occurs and the surface potential decreases (figure 6).

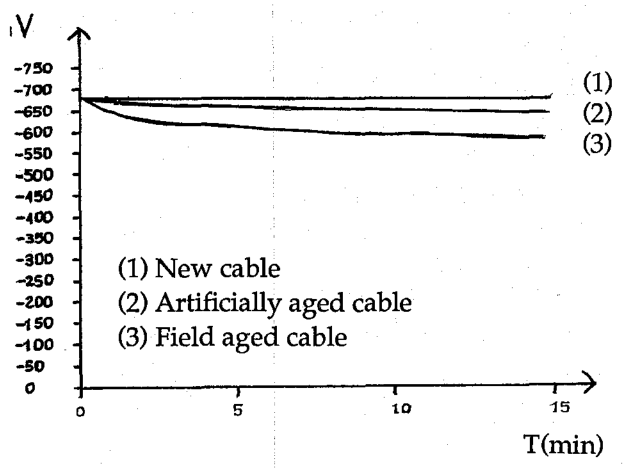

figure 6
Surface potential measurements recorded in function of time for new and aged polyethylene samples
N : new cable , AA : artificially aged cable , FA : field aged cable

The artificially aged cable (AA) presentes a slight decay of surface potential, therefore , a lower resistivity. Its behaviour is an intermediate between those of new and field aged cables. The resistivity of the polyethylene after a long duration test is smaller than the one of the new material but higher than the one of the field aged insulation.
These results are in agreement with the membrane potential measurements.
Membrane potential measurements and surface potential measurements both indicate a deviation from the insulating behaviour of the field aged cables. Therefore , the modification of the ionic and the electrical conductibility of polyethylene with ageing seems to be correlated with its chemical modifications since the behaviour of the new material differs from that of the aged one.

III-4 *Physico-chemical modifications responsible for the electrical changes noticed*

By the use of surface diagnostic techniques such as XPS, IR microscopy and contact angle measurements an attempt has be made to correlate the modifiation of the observed electrical properties noticed, to physico-chemical modifications.

XPS analysis allowed us to detect oxygene traces at the surface of field aged polyethylene as well as a slight increase of the oxidation of the semi-conducting shields. The O/C ratios calculated are presented in table I.

Table I
O/C ratios for new, field aged and artificially aged cables

	New Cable	Artificially Aged Cable	Field Aged Cable
External Semi-conductor	0,044	0,036	0,04
External Dielectric	0,013	0,004	Traces
Bulk Dielectric	0	0,005	Traces
Internal Dielectric	0,006	0,003	Traces
Internal Semi-conductor	0,040	0,036	0,04

Oxidation at the vicinity of the semi-conducting shields is more rapid for artificially aged cable than for field aged cable while the bulk of insulating material seems to undergo no change.
According to these results the contact angle measurements (carried out with an image processing system elaborated in the laboratory and patented [11]) pointed out a slight increase of wettability for an aged polyethylene. The surface tension of new and aged materials are presented in table II.

Table II
Surface tension for new, field aged and artificially aged cables

	Water Angle	DMF* Angle	γ_d (mJ/cm2)	γ_p	γ_s
New Cable	91,8	78,9	14,91	5,81	20,73
Artificially Aged cable	90,8	80,2	12,69	7,27	19,97
Field aged Cable	89,0	78,2	13,33	7,83	21,16

* Dimethyl-formamide

The polar component of the surface tension increases for an aged material which could point out that the polar groups present on the surface of the sample may result from an oxidation mechanism of the bulk material.

In order to identify these polar groups , IR microscopy was performed. The characteristic Infra- red bands of polyethylene are well known ; so only the range of 2200 to 1500 cm-1 is presented figure 7.

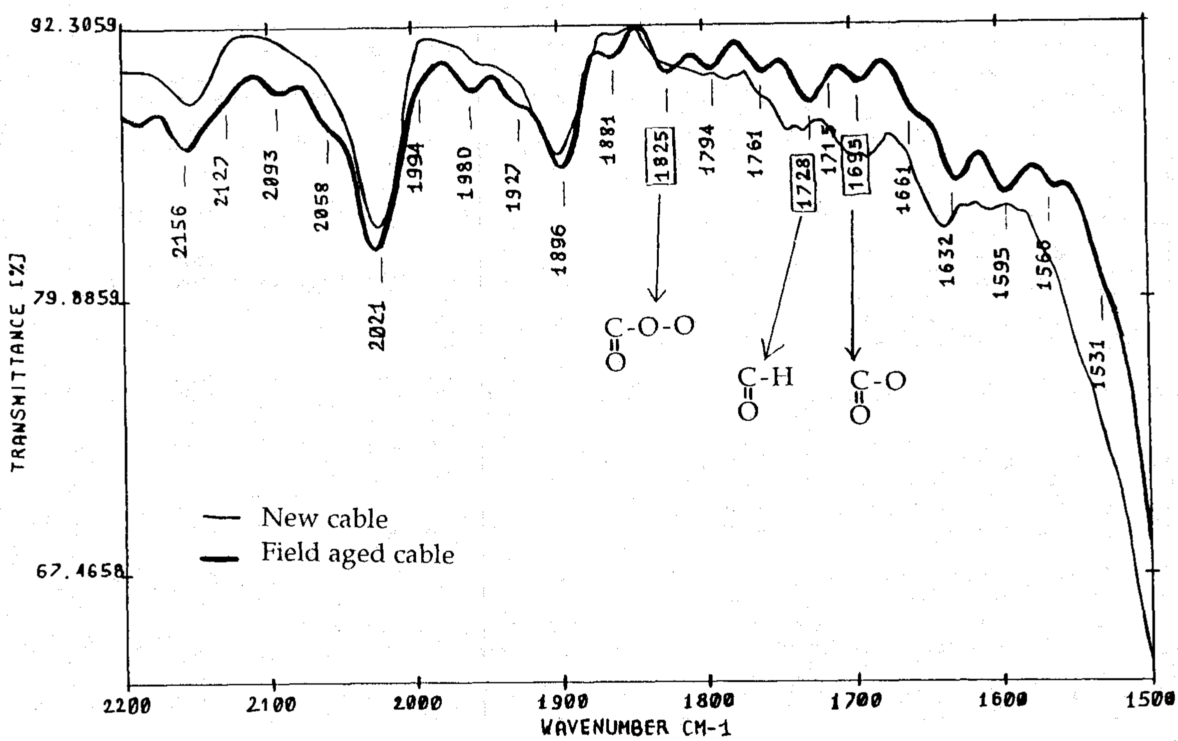

figure 7
IR spectra of new and field aged polyethylene

For the field aged polymer, absorption bands at 1595 cm-1, 1728 cm-1 and 1825 cm-1 are attributed to following groups (1595 cm-1 : COO^-, 1728 cm-1 : COH , 1825 cm-1 : CO-OO). Thus , the electrical modifications observed at presented above (ionic transport phenomenon and surface potential decay) can be induced by these new functions. In this way , the ionic transport through the dielectric material membrane appears to be generated by oxidation by-products and in particularly by carboxylic acid groups. These groups would behave as ionic carriers species and could be responsible for the ionic transfer phenomenon.

IV- Conclusion :

New analytical techniques are needed to detect the slight modifications of the electrical and chemical properties of an aged dielectric material. That is the reason why we chose to performe original methods such as membrane potential measurements and surface decay potential measurements. The former allowed us to point out an ionic transport of H^+, K^+ and Na^+ through field aged membrane. This phenomenon is correlated to appearence of polar groups detected by the use of contact angle measurements. Furthermore, IR microscopy permits us to identify new function such as carboxylic acid groups.

It is well known that membranes used in ion selective electrodes are constituted by an active sensor such as a simple insoluble salt, a chelate or ion exchange resine and by an inactive polymeric support [12]. By analogy with the composition of such membranes one can conclude that this ionic transfer could be due to the presence of organic carriers. Carboxylic acid groups pointed out by IR-microscopy and produced by the breaking of polymeric chains followed by an oxydation , would behave as organic carriers. They could be responsible for the ionic transfer phenomenon which occurs in aged materials. Therefore , the metallic impurities diffusion pointed out by NAA in aged insulators could be due to the presence of oxidation by-products. This could explain the diffusion of impurities from the semi-conducting shields through the dielectric material. Moreover, surface potential measurements have shown a less slow dissipation of charges injected at the surface of field aged polyethylene than for the new one. The modification of insulating properties lead to a less resistive polymer with ageing.

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