Pure and Applied Geophysics

Second Generation of Lead-lead Chloride Electrodes for Geophysical Applications

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Abstract—A large number of geophysical applications need long-term telluric recordings. In order to realise it correctly, the use of very stable electrodes is necessary. The study of the potential variations of Pb-PbCl$_2$ electrodes as a function of both the ionic composition and the pH of its electrolyte allows one to chose the optimal working criteria. The best stability and the minimum noise for the potential are obtained for a solution saturated in both salts PbCl$_2$ and KCl, or PbCl$_2$ and NaCl, in the presence of additional non-dissolved salts, with a pH from 4 to 5. The study of the salts diffusion between the inside of the electrode and the outside medium allows one to compute the time span over which the potential remains stable (t_D time of dissaturation), and to know how to increase it. Two solutions are possible. The first one is to increase the electrode length, because t_D is proportional to the length squared. The second one is to reduce the exchanges of salts with the external medium, by using an electrode with a narrow channel. In this case, t_D is proportional to the quantity of non-dissolved salt in the electrode and to the internal electrical resistance of the electrode. The fabrication of this new electrodes design with a channel is described.

Key words: Telluric survey, magnetotelluric survey, lead-electrodes, electrode chemistry, long-term stability.

1. Introduction

Impolarizable electrodes are used to measure the potential differences between two points of ionic conductors (encountered in chemistry, biology, and, in our case, geophysics). They are essentially made up of a metal in contact with a salt solution of this metal. Between the various metal-salt couples, we have retained Pb-PbCl$_2$ (PETIAU and DUPIS, 1980).

In the present study we make a detailed analysis of the potential of Pb-PbCl$_2$ electrodes potential in terms of the concentrations of the principal salt (PbCl$_2$), of the auxiliary salt (KCl or NaCl), and of the internal pH. The aim is to find domains where this potential is particularly stable. We also study the salt diffusion between the inside of the electrodes and the external medium in order to estimate and improve their long-term stability in the ground.

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Let us recall that the main part of the potential of an electrode is given by the Nernst formula:

$$E = E_0 + \frac{RT}{nF} \ln a_{M^{+n}} \tag{1}$$

$a_{M^{+n}}$ activity of the metal ion (concentration which actually acts in solution)

E_0 standard potential at 25°
R Constant of the perfect gas
T absolute temperature
F Faraday constant
n metal valency

with $RT/F = 25.7$ mV at 25°C.

An *electrode of the first kind* is essentially made of a metal in contact with a solution of a salt of this metal. If the metal salt, for example, MX_n (M^{+n} cation, X^- anion) is very weakly soluble, and if the solution is saturated with a supplement of non-dissolved salt, adding another salt containing the same anion X^- makes an *electrode of the second kind*. The concentration of the M^{+n} ions is then defined by the relation:

$$[M^{+n}] = K_s/[X^-]^n \tag{2}$$

where K_s is a constant (the solubility product) and $[X^-]$ is the total concentration of the X^- ions in the solution originating from both the metal salt and the added salt. When the metal salt is very weakly soluble, the addition of a second salt is indeed necessary in order to obtain a correct conductivity of the electrolyte.

Let us underline that the presence of other ions in the solution can also modify the electrode potential, (1) by changing the cation concentration or the activity of the metal $[M^{+n}]$ (hydration, formation of complexes), (2) by oxidising or reducing effects, (3) by modifying the pH. Moreover, in the presence of a cation of a metal which is less oxidisable than that of the electrode, this less oxidisable metal would deposit on the electrode metal and change the nature of the electrode.

Furthermore, when the electrode potential is measured with respect to a reference, a diffusion potential is generally added (BARD and FAULKNER, 1980; ATKINS, 1982; CLERC et al., 1998).

2. Potential as a Function of PbCl₂ and KCl Concentrations

2.1 Method of Measurement

This experiment, apparently quite simple, requires precautions to be carried out correctly.

We might start using a lead wire placed in a liquid electrolyte and progressively increasing the salt dose, the potential being measured with respect to a reference electrode (saturated in $PbCl_2$ and KCl). Unfortunately, the measurements are then scattered for the following reasons:

—The stabilisation time of the potential can be very long, especially for weak doses of salt. One needs then to use a separate electrode for each combination of doses.

—Let us consider a standing electrolyte column and a lead wire in contact with this solution only through a loop located at a known height (the rest of the wire being insulated until the exit from the electrolyte). One observes that the potential varies with the height of the loop. For a 10 cm column height, the potential difference between the top and the bottom may vary from 5 to 10 mV. Furthermore, if some salt remains non-dissolved, the potential value changes abruptly when the lead comes in contact with the salt sediment.

—If the solution is stirred in order to be homogenised, the electrolyte is oxygenated and the potential is also modified.

In order to obtain good measurements, one must prepare and use true electrodes (a simplified version of the one represented, Fig. 8 in section 6). To avoid the drawbacks of a liquid electrolyte (see above), this electrolyte should be fixed by a gel or a mineral powder (MEUNIER 1962; PETIAU and DUPIS, 1980). We use a clay mainly composed of kaolinite and illite (potter clay), compatible with an acidic electrolyte, and prepare a thick mud. The adsorption forces (which keep the electrolyte at the surface of the grains) are far more important than the gravity forces, and the medium is very homogeneous. Moreover, any supplement of non-dissolved salt is dispersed throughout the volume. As will be defined in section 3, the acidity of the mud is chosen at pH 4. A wooden porous plug closes the electrodes and provides the outside contact.

The tested electrodes and the reference electrode are placed in a box, on plastic foam soaked with a saturated KCl solution. The electrodes must be long enough (the distance between the lead and the bottom of about 10 cm) so that the internal concentration is not disturbed during the measurements by the diffusion of the salts from the foam.

Finally, as the electrodes with weak doses of salts are poorly conducting, one must use a voltmeter with a very high input resistance. The measurements are made at about 20°C.

A set of 23 test electrodes was prepared with variable combinations of concentrations of $PbCl_2$ and KCl, from a zero concentration to saturation ($PbCl_2$ 10.9 g/l, KCl 355 g/l), and also beyond saturation with additional non-dissolved salt. The experiments were repeated several times.

2.2 Results of Measurements

Figures 1 and 2 show the potential curves as a function of the concentrations of $PbCl_2$ and KCl. The points indicate the experimental values obtained after 48 hours
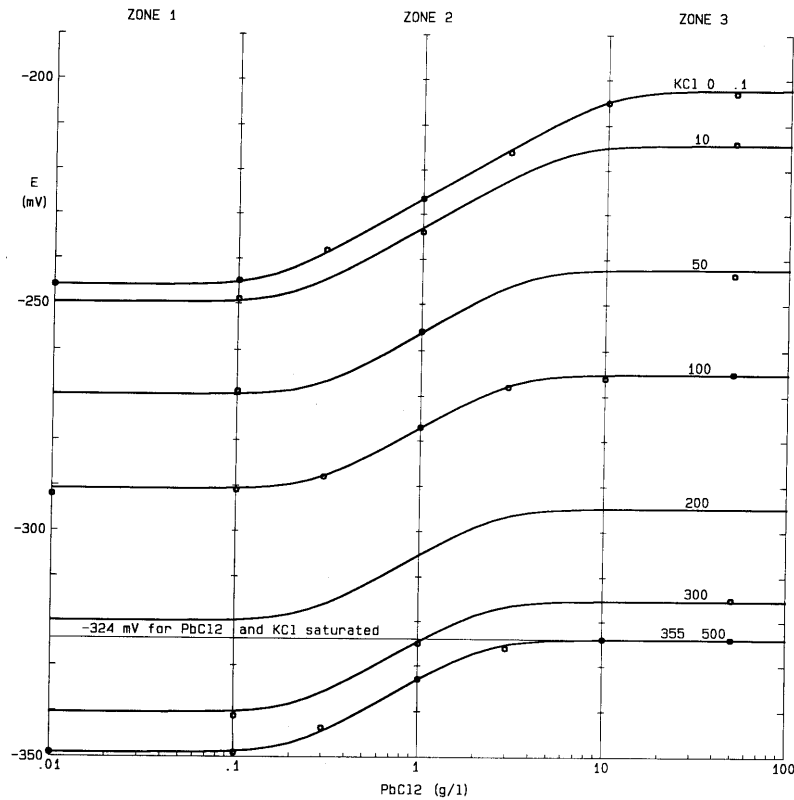
Figure 1
Electrode potential as a function of $PbCl_2$ concentrations for various concentrations of KCl, indicated in g/l.

of stabilisation, and the curves are drawn using the method described thereafter. The obtained curves are very different from the ones, *a priori* expected, for second kind electrodes.

Figure 1 clearly shows three different zones. In the first zone ($PbCl_2 < 0.15$ g/l) the potential remains constant as $PbCl_2$ concentration increases. Furthermore, the potential is larger than that corresponding to the Pb^{++} ions provided by $PbCl_2$. One can conclude logically that there is a self-dissolution of the metal favoured by the acidity of the medium (pH 4). In the second zone ($PbCl_2$ varying from 0.15 g/l to 3–10 g/l) the potential increases with the provided quantity of $PbCl_2$. Finally, in the third zone ($PbCl_2 > 3$–10 g/l), the potential again remains constant, after saturation is reached (for example, for KCl = 0 we retrieve the known value of the solubility of $PbCl_2$ in water, which is about 10 g/l). When the KCl concentration increases, the potential decreases in the three zones, and not only in the third one where the saturation is reached, which should be emphasised.
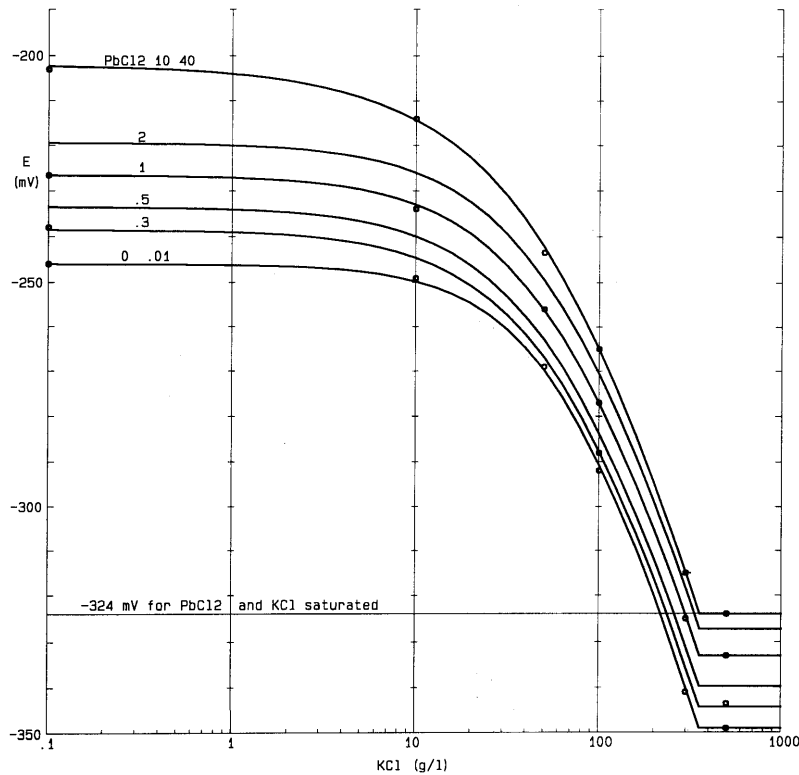
Figure 2

Electrode potential as a function of KCl concentrations for various concentrations of PbCl$_2$, indicated in g/l.

Considering that the solubility product $K_s = 1.7 \times 10^{-5}$ for PbCl$_2$ and the activity coefficient is 0.58 for KCl at saturation (PAULING, 1963; HARNED and OWEN, 1958) we have:

$$[Cl^-] = (355/74.6) \times 0.58 = 2.76 \text{ mol/l}$$

and

$$[Pb^{++}] = 1.7 \times 10^{-5}/2.76^2 = 2.23 \times 10^{-6} \text{ mol/l}.$$

This corresponds to a value of 6.2×10^{-4} g/l for the PbCl$_2$ concentration and this is an upper bound because the real activity of $[Pb^{++}]$ can be weaker. For saturated KCl, the potential should be independent of PbCl$_2$ concentration beyond the value of 6.2×10^{-4} g/l, whereas the measurements show that it depends on PbCl$_2$ up to about 3 g/l. To conclude, the computation using the solubility product of PbCl$_2$ cannot be used.

On the other hand, as shown in Figure 2, near the saturation in KCl, the slope appears to decrease as $[Cl^-]^{4.3}$, while with PbCl$_2$, the slope should be as $[Cl^-]^2$.

This leads to the thought that when the concentration in Cl^- ions is sufficient, the dissolved lead chloride is transformed into complexes like $PbCl_3^-$, $PbCl_4^{-2}$, or more generally $PbCl_b^{2-b}$. These complexes are only partially ionised according to the equilibrium:

$$PbCl_b^{2-b} \leftrightarrow Pb^{++} + b\ Cl^-. \tag{3}$$
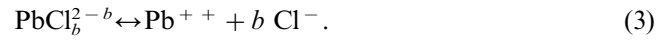
Thereafter one obtains, with the following notations:

K_i ionisation constant
K_s solubility product
α ionisation coefficient
$a_{Pb^{++}}$ Pb^{++} activity
a_{Cl^-} Cl^- activity (emanating from KCl or $PbCl_2$)
$PbCl_b^{2-b}$ concentration of the complex produced from the dissolved $PbCl_2$
P_{nd} activity of the non-dissociated complex part
P_s concentration at saturation of the dissolved complex
P_d concentration of the complex corresponding to self-dissolution

$$K_i = \frac{a_{Pb^{++}}(a_{Cl^-})^b}{P_{nd}} \tag{4}$$

with

$$a_{Pb^{++}} = \alpha\ PbCl_b^{2-b} \tag{5}$$

and

$$P_{nd} = (1 - \alpha)PbCl_b^{2-b} \tag{6}$$

K_i becomes

$$K_i = \frac{\alpha(a_{Cl^-})^b}{1 - \alpha} \tag{7}$$

and then

$$\alpha = \frac{K_i}{(a_{Cl^-})^b + K_i}. \tag{8}$$

Thus, α is independent of $PbCl_b^{2-b}$ and depends only on a_{Cl^-}. If K_i is small or a_{Cl^-} is large:

$$\alpha \approx \frac{K_i}{(a_{Cl^-})^b} \ll 1 \tag{8a}$$

where the complex is at saturation, $PbCl_b^{2-b} = P_s$, and K_s intervenes and is equal

to $a_{Pb++}(a_{Cl-})^b$. Using (5), the obtained value for K_s is $\alpha\, P_s(a_{Cl-})^b$ and, using (8), P_s can be expressed as:

$$P_s = \frac{K_s}{K_i}\frac{K_i + (a_{Cl-})^b}{(a_{Cl-})^b}.$$ (9)

If K_i is weak or if a_{Cl-} is large:

$$P_s \approx K_s/K_i.$$ (9a)

P_s becomes a constant and then it does not depend on the supplied quantities of $PbCl_2$ or Cl^-. Indeed, if a_{Cl-} increases, then a_{Pb++} (and also E from formula (1)) decreases, however due to the variation of α, Cl^- is eliminated and P_s remains unchanged.

For lead electrodes, $E_0 = -126$ mV and the Nernst potential (1) is written:

$$E = -126 + 12.85 \ln a_{Pb++}.$$ (10)

The potential measured with respect to a hydrogen reference electrode is for a *saturated $PbCl_2$ and KCl electrode*, $E = -314$ mV. The following quantities can then be calculated. From (10) one obtains.

$$\ln a_{Pb++} = (126 - 314)/12.85 \quad a_{Pb++} = 4.43 \times 10^{-7}\,\text{mol/l}$$

$$Pb^{++}\ \text{dissolved} = P_s = 2.5/278 \quad P_s = 0.009\,\text{mol/l}$$

then

$$\alpha = 4.43 \times 10^{-7}/0.009 \quad \alpha = 4.9 \times 10^{-5}\ (\alpha\ \text{is very weak}).$$

The activity of Cl^- provided by KCl (already computed) is:

$$a_{Cl-} = (355/74.6) \times 0.58 \quad a_{Cl-} = 2.76\,\text{mol/l}$$

4.3 ions of Cl^- are used in the complex for every Pb^{++} ion, so:

$$4.3 \times 0.009 \approx 0.04\,\text{mol/l}.$$

The real activity of Cl^- is $2.76 - 0.04 = 2.72$ mol/l. One obtains, with (8a):

$$K_i = \alpha\, a_{Cl-} = 4.9 \times 10^{-5} \times 2.72^{4.3} \quad K_i = 3.62 \times 10^{-3}$$

and with (9a)

$$K_s = p_s \times K_i = 0.09 \times 3.62 \times 10^{-3} \quad K_s = 3.26 \times 10^{-5}.$$

Finally, using (5) and (8) we obtain for the expression of a_{Pb++}:

$$a_{Pb++} = \frac{K_i(PbCl_b^{2-b})}{K_i + (a_{Cl-})^b}.$$ (11)

2.3 Smoothing Functions

Figure 1 indicates that the transition at the junction between two zones is progressive. This is the general case when the variation of a physical quantity (F) is described by two different functions ($F1$ and $F2$) in two contiguous domains; the transition is always more or less smoothed off. Two cases are to be considered, depending on whether the solution to retain is the greatest or the smallest of the functions $F1$ and $F2$. For $F1$ and $F2 > 0$, this leads to the following expressions:

$$\text{Smoothing when retaining the maximum} \quad F_{\max} = (F1^q + F2^q)^{1/q}. \quad (12)$$

$$\text{Smoothing when retaining the minimum} \quad F_{\min} = F1 \cdot F2/(F1^q + F2^q)^{1/q}. \quad (13)$$

The q parameter allows one to adjust the round off of the transition. The round off is largest when q is smaller. In our case $F_{\max}$ must be used between zones 1 and 2, and $F_{\min}$ between zones 2 and 3.

2.4 Computation of the Potential as a Function of PbCl₂ and KCl Concentration

We are now going to search for a formula which will allow us to express the activity of Pb^{++}, and afterwards compute the corresponding potential with expression (10). If we use straightforwardly the relation (11), we do not find the exact experimental values, i.e., we find that K_s and K_i vary with the concentrations. This relation must then be modified. In order to be usable, the formula we are looking for is to be expressed as a function of raw concentrations of $Pb^{++} = PbCl_2(g/l)/278$ and $Cl^- = KCl(g/l)/74.6$ (278 and 74.6 molar mass of the two salts). In such condition, it would not be necessary to introduce corrections due to activity or partial ionisation, which are very difficult (or impossible) to be correctly determined when the concentrations are large and for a complex medium where secondary compounds are formed. The coefficients and the exponents of this formula take into account these effects globally, since they are precisely adjusted in such a way as to give the measured potentials. After some trials, we chose the following formula:

$$a_{Pb^{++}} = \frac{G[Pb^{++}]^a}{[1 + C^r[Cl^-]^{br}]^{1/r}} \quad (14)$$

with

$a_{Pb^{++}}$	activity of Pb^{++} ion (mol/l)
$[Pb^{++}]$	raw concentration of Pb^{++} provided by $PbCl_2$ (mol/l)
$[Cl^-]$	raw concentration of Cl^- provided by KCl (mol/l)
G, C	coefficients
a, b	exponents
r	smoothing parameter as a function of KCl.

For KCl = 0 this formula becomes:

$$a_{Pb^{++}} = G[Pb^{++}]^a. \tag{14.1}$$

This is the expression corresponding to a first kind electrode, using only the metal salt (zone 2 and curve KCl $= 0$ of Fig. 1).

The validity domain of formula (14) is limited by self-dissolution (zone 1) and saturation (zone 3). The limit corresponding to the self-dissolution (Pd) (between zones 1 and 2 is independent of KCl, with Pd about 5.4×10^{-4} mol/l, corresponding to 0.15 g/l of $PbCl_2$. But the $PbCl_2$ saturation limit (P_s), at the boundary between the zones 2 and 3 decreases at KCl increases, and must tend toward a limit when Cl^- becomes very large, as relation (9a) shows. We express this relation between P_s and $[Cl^-]$ by:

$$P_s = 0.0154 \left(\frac{27.2 + [Cl^-]}{1 + 43.5[Cl^-]} \right)^{0.28} \tag{15}$$

where KCl is very large (in fact beyond the Cl^- provided by KCl at saturation), P_s tends towards 5.4×10^{-3} mol/l, which corresponds to 1.5 g/l of $PbCl_2$. However, this limit cannot be fixed accurately because the greatest concentrations of Cl^- are not reachable. The most important conclusion is that, with a self-dissolution corresponding to 0.15 g/l of $PbCl_2$, zone 3 never reaches zone 1 and there is always a zone 2 where the potential remains a function of the provided $PbCl_2$, whatever the Cl^- concentration is.

The parameters of the formula (14) have been adjusted by a systematic search on a computer, in such a way as to reproduce the measured value. The smoothing parameter r as function of KCl is to be adjusted in each zone 1, 2, 3, $(r1, r2, r3)$. We obtained the following values:

G	C	a	b	q	$r1$	$r2$	$r3$
0.0362	1.55	0.8	4.6	4	0.280	0.235	0.227

The G coefficient allows us to fix the computed values into the scale of standard potentials. Thus we do obtain -324 mV for an electrode with saturated $PbCl_2$ and KCl.

The computation steps are the following. For each dose of KCl we compute the values of $a_{Pb^{++}}$ first in zones 1 and 3 (where $a_{Pb^{++}}$ is independent of $PbCl_2$), then in zone 2 (where $a_{Pb^{++}}$ varies with $PbCl_2$). The smoothing formulae are applied between two successive zones (F_{max} between 1 and 2, then F_{min} between 2 and 3). Therefore the method allows to compute $a_{Pb^{++}}$, and the corresponding potential, without discontinuity, for all values of $PbCl_2$ and KCl.

With NaCl (instead of KCl), and both salts NaCl and $PbCl_2$ saturated, the electrode potential is -297 mV. At saturation, the activity coefficients of KCl and NaCl are respectively 0.58 and 0.99 (HANDBOOK OF CHEMISTRY AND PHYSICS, 1959; PAULING, 1963). Activity of Cl^- with KCl is $0.58 \times 355/74.6 = 2.76$ mol/l, and with NaCl $0.99 \times 361/58.5 = 6.2$ mol/l. Therefore, the potential electrode with NaCl should be weaker than with KCl. However, the contrary is measured. One must then conclude that the presence of Na^+ cations instead of K^+ cations modifies the equilibrium of the formed Pb^{++}, Cl^- complexes.

2.5 Conclusion

With KCl, the concentration of Pb^{++} provided by $PbCl_2$ is modified by the exponent $a = 0.8 < 1$. This suggests that the activity decreases when the concentration increases.

Obtaining such a result, which is in very good agreement with the experimental values, confirms that in the electrolyte, with a supplement of Cl^- provided by KCl, Pb^{++} ions form a mixture of complexes of $PbCl_b^{2-b}$ type. The number of Cl^- ions (b) contained in the complex increases with the concentration in Cl^-. At the limit, for a very high concentration, larger than that provided by KCl at saturation, the mixture of complexes has an effect equivalent to a mean of $4.6\ Cl^-$ ions for one Pb^{++} ion. For the saturated KCl the equivalent effect is $4.3\ Cl^-$ ions for one Pb^{++} ion.

As the potential strongly varies as a function of the concentration of the salts, it is necessary to keep the concentrations stable in order to have a stable potential. The best way to obtain this result is to use a saturated solution with additional non-dissolved salts for each of them (HEMPFLING, 1977). We will more thoroughly study this long-time stability in section 5.

3. The Electrodes Behaviour as a Function of Internal pH

3.1 Aim of this Study

For our first electrodes the acid or basic reaction in the internal medium was not controlled; it was simply determined by the components of the electrolyte and the absorbent material (plaster or clay):

$PbCl_2$	KCl	plaster	pH 7.1	clay	pH 6.6
$PbCl_2$	NaCl	plaster	pH 6.5	clay	pH 6.1.

It must be noted that such is the case for most types of electrodes; the pH is not adjusted, and is determined also by the used salts and the added absorbent materials (if any).

The pH parameter is very important and we will study here its influence on the potential, on the noise, and on the temperature coefficient, in order to search the value giving the highest stability of the electrodes.

3.2 Preparation of the Electrodes and Methods of Determination of the pH Sensibility

A set of electrodes with 14 values of pH ranging from 0 to 10 has been first realised; afterwards more values of pH have been added to better define the parameters, changes where these changes are rapid. Two identical electrodes have been made for each value of pH in order to measure the noise. As shown in the previous chapter,

in our experiments the electrolyte is saturated with an extra amount of non-dissolved salts ($PbCl_2$ and KCl), and powder clay is added to form thick mud. For each experiment a fraction of the water is replaced by a solution of hydrochloric acid or potassium hydroxide (HCl or KOH) in order to obtain the wanted pH. Due to the presence of the clay, this pH takes a long time to stabilise and must be measured and adjusted a few days before using the mud in the electrodes.

As we need a time-span of about a month for the measurements, a PVC disk with a narrow channel (ϕ 1.5 mm and L 10 mm) is set up at the bottom of the electrodes (like Fig. 8) to limit the exchanges with the outside. As the KCl is saturated inside the electrode, the electrical resistance of the channel is still weak ($\sim 400\ \Omega$) while the protection is very efficient. The electrodes are set up vertically on plastic foam soaked with a saturated KCl solution. All the potentials are measured with respect to an older (stabilised) reference electrode with an internal pH of 4. The whole device is placed in an oven at a temperature first fixed at 25°C. That allows us to measure two parameters as a function of pH: the potential (the average of the potentials of the two electrodes with the same pH), and the noise (the differences of potential for these two electrodes with the same pH). Then we measure the temperature coefficient of the electrodes by varying the oven temperature. The potentials are measured once a day, spanning a month. These daily measuarements allow us to estimate the noise for a period (T) of two days.

For values of pH from 1 to 6, potential stabilises in 1 to 3 days, but for very acid medium (pH < 1) or basic ones (pH > 7.5) the stabilisation is not yet reached after a month. This drift is due to the variation of pH with time. To take this into account, the electrodes are dismantled after 30 days of measurements, and pH are measured once more. These final values are the ones which are used to draw the following curves.

3.3 Results of Measurements for the KCl Electrodes

a. Potential. The first curve in Figure 3 shows the potential variation as a function of pH, on the 30th day of the experiment. In the previous section we saw that in an acid medium complexes with Cl^- ions are formed. The H^+ ions do not participate in the equilibrium described by formula (3) and this explains the very weak variation of the potential with pH, from neutrality to pH 3. For pH < 3, the potential slowly increases with acidity until pH $\approx$ 1. For a very acid medium (pH < 1) the concentration in Cl^- ions from HCl is no more negligible compared with that due to KCl; the total concentration of Cl^- increases and the potential decreases.

When the medium becomes basic, i.e., for pH larger than 7.3, the potential sharply decreases. The nature of the electrode changes with the presence of OH^- ions, and a lead hydroxide is probably formed. The measurements made up to pH 10 (not represented on Figure 3 in reason of the scale) show that the slope remains
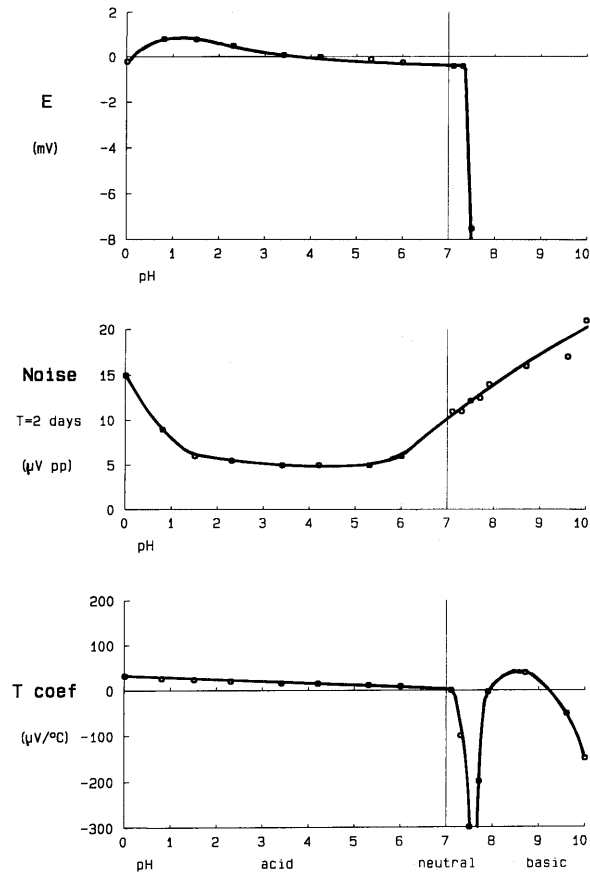
Figure 3
Potential, noise and temperature coefficient of PbCl$_2$, KCl electrodes as a function of pH.

constant and that the potential decreases by about -30 mV per unit of pH. This proves that is not Pb(OH)$_2$ which intervenes: for an increase of one unit of pH, the OH$^-$ concentration is multiplied by 10, which would give a slope of $-12.85 \ln(10^2) = -59.2$ mV.

We have carried out a few more experiments in basic media with variable doses of KCl, which indicate that the potential also varies with the Cl$^-$ concentration. When the KCl concentration approaches saturation, the potential decreases by 34 mV when KCl concentration is doubled. This demonstrates that there is a mean value of $34/12.85 \ln 2 = 3.8$ Cl$^-$ ions for one Pb^{++} ion in the compound. A mixture of (PbCl$_n$OH)$^{1-n}$ complexes is then formed with an equivalent effect of a mean value of 3.8 for n. These complexes are similar to those formed in an acid medium, although here a Cl$^-$ ion is replaced by an OH$^-$ ion.

To conclude on the potential, to have the best potential stability, we must choose an acid medium with a pH varying from 3 to 6.5. Neutrality is to be

avoided because it is too close to the very strong potential variation beginning at pH 7.3.

b. Noise. Performing measurements every day during a month makes it possible to estimate the noise for a period of $T = 2$ days, for each couple of electrodes at the same pH. This noise is expressed in μV_{pp} (see the next section). The noise is the lowest in an acid medium (pH between 2 and 6), which is then the domain to retain. Noise is considerably more important in very acid medium and in basic medium.

c. Temperature coefficient. The temperature coefficient is very weak throughout the acid zone. It regularly decreases from 30 $\mu V/°C$ for pH 0 to some $\mu V/°C$ for pH 7. When the medium becomes basic this coefficient becomes strongly negative, with a minimum of about -400 $\mu V/°C$ for pH 7.6, and thereafter it becomes very variable. It is zero for pH 7.2, however this pH value cannot be retained because of the strong potential variation at pH 7.3.

Conclusion. One cannot retain a basic medium because a very weak variation of the internal pH leads to a large potential variation. We tried to use a pH buffer to stabilise the pH (for example at 7.3 to have a null temperature coefficient) but observed that the salts added as a buffer make electrodes unstable and therefore this solution is not applicable.

The best working domain is then located between pH 4 and 5: the potential variation is very weak as a function of pH, the noise is the lowest (5 μV_{pp}), the temperature coefficient is not null but very weak (~ 20 $\mu V/°C$). Moreover, as stated above, for that domain of pH, the potential is stabilised 1 or 2 days after the electrodes have been built.

Measurements for NaCl electrodes. The same measurements have been carried out replacing potassium chloride with sodium chloride and using the sodium hydroxide in order to achieve a basic medium. The reference for the potential measurements is a NaCl electrode of pH $= 4$. Figure 4 illustrates that the curves are slightly different from those of KCl. In an acid medium *the potential* is still more stable than that with KCl; it is practically constant between pH 2 and 6. The sudden decrease starts at pH 6.3 and not at pH 7.3 as was the case with KCl. *The noise* is minimum in a narrower domain, i.e., between pH 3 and 6 (5 μV_{pp} as for KCl). *The temperature coefficient* varies between 230 $\mu V/°C$ at pH 2 and 220 $\mu V/°C$ at pH 6, which makes a significant difference between the two chlorides. We again found an abnormal behaviour similar to that observed with KCl, which starts at pH 6.3, corresponding to the decreasing point of the potential.

The domain of pH 4 to 5 can be retained as in the case of KCl electrodes. The potential is also stabilised 1 or 2 days after the electrodes have been built. The temperature coefficient is 220 $\mu V/°C$. This value is still small compared to temperature coefficients of other electrodes: 700 to 900 $\mu V/°C$ for copper electrodes or -400 to 600 $\mu V/°C$ for various kinds of silver electrodes (CLERC et al., 1998).
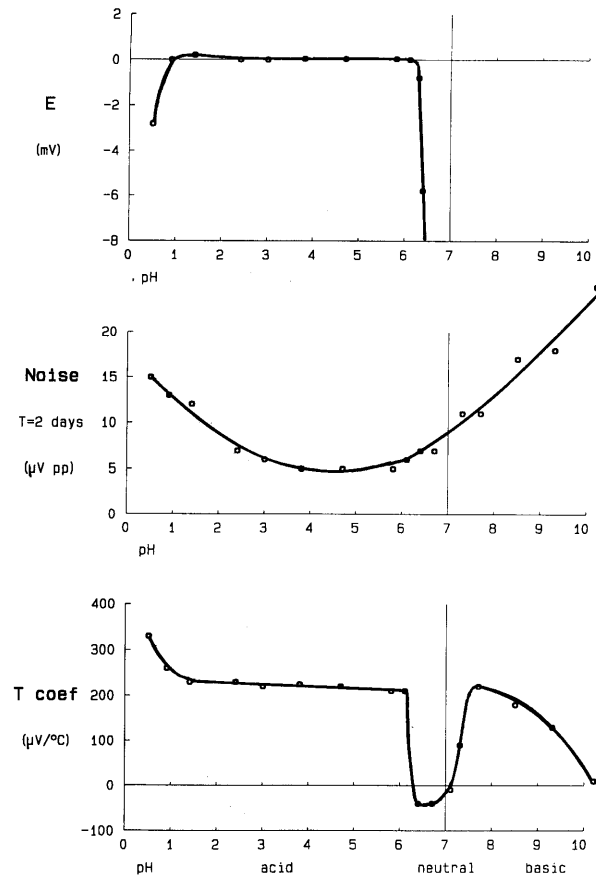
Figure 4
Potential, noise and temperature coefficient of $PbCl_2$, NaCl electrodes as a function of pH.

4. Noise of Electrodes

Adopting the optimal conditions to build the electrodes (i.e., saturated solution with additional non-dissolved salts, pH 4 to 5, thick and homogeneous mud), the spectrum of the intrinsic noise of the electrodes has been measured.

The experiment was conducted in the same conditions as in the previous section. The entire experimental set is put into the oven at a constant temperature. Potential differences between two electrodes are amplified and digitised with a sampling depending on the studied periods range. The noise spectrum is determined by FFT or numerical filtering. We have tried hard to determine noise values for the long periods; these measurements are difficult because they are time-consuming (a minimum of 10 to 20 times the considered period). However, the simultaneous recording of the noise for several pairs of electrodes allows us to shorten this time span and to check the homogeneity of the measurements.

The noise is relative to a pair of electrodes. It is not expressed in the form of a noise density ($\Delta F = 1$ Hz), but as the mean peak-to-peak value for $\Delta F = F$ (PETIAU and DUPIS, 1980). This is very useful to directly compare the noise amplitude with the amplitudes of the geophysical signals measured with the electrodes. The relation between the two noise expressions is:

$$\text{Noise}(V_{pp}, \Delta F = F) = \text{Noise}(V_{rms}, \Delta F = 1 \text{ Hz})2\sqrt{2}\sqrt{F}.$$

Figure 5 displays the results of the measurements. The noise for the electrodes with plaster and NaCl (first generation, PETIAU and DUPIS, 1980) is also shown for comparison (curve a). The second generation electrodes (curve b) present a much reduced noise. Furthermore, the improvement of the amplifiers (LTC1052) allows measurement of much weaker noise levels. For this second generation we have not found significant differences between the KCl electrodes and the NaCl electrodes. We notice that a change of slope occurs around 10–30 minutes and the noise increases for longer periods.

The comparison between the two generations is interesting. For the first generation, the experiment was carried out without temperature control, although this cannot affect noise level within the period ranges studied at that time (< 1000 seconds). The composition of the internal medium was less homogeneous when using plaster than with clay-mud. Indeed, when preparing the electrodes, the plaster was poured in a liquid state into the electrode tube and the non-dissolved salts could more or less sediment before solidifying. The main explanation however is given by the study of the potential as a function of pH, in the previous section. Using NaCl and plaster, the pH was about 6.5, value confirmed by the
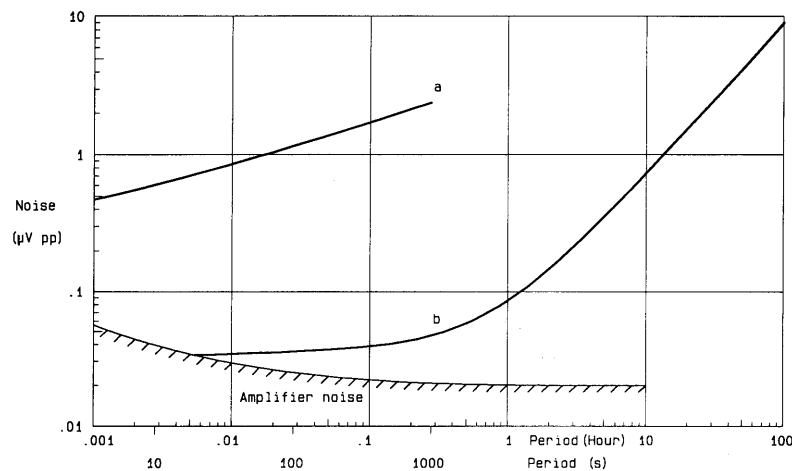

Figure 5

Noise electrodes as a function of the period: (a) First generation with NaCl and plaster; (b) Second generation with NaCl or KCl, pH 4 to 5 and clay mud.

temperature coefficient of -40 $\mu V/°C$ of these first generation electrodes. The working point was then in the very unfavourable domain in which the potential strongly varies as a function of pH (Fig. 3). Reducing pH in plaster is not possible because it contains calcium carbonate, which decomposes when adding acid. Mud can be used because it is compatible with an acidic medium.

5. Long-term Stability

5.1 Adaptation to the Applications

For usual magnetotelluric prospecting, which requires a few hours of recordings, the long-time stability is not very important. In this case we especially look for an easy set-up and a quick stabilisation of the electrodes. To correctly obtain the diurnal variation and slower variations (within a few days), the recording time span should be a few weeks or even a few months. For other applications (evolution of the spontaneous polarisation or of the resistivity in a given site, search for signals related to seismic activity), the electrodes must keep their stability for months or years. As was noted, in order to keep a stable potential, it is at least necessary to use saturated solutions with additional non-dissolved salt.

5.2 Electrodes in Dry Ground

If the ground is dry it absorbs the internal solution of the electrode by capillarity, and some salts deposit in places where the solution can evaporate. At the beginning this process takes place outside of the electrode and thereafter continues inside it, because air can penetrate the dried pores even if salts have deposited. Thus, inside the electrode, the solution is saturated at the beginning and remains saturated. The potential changes only when there is no more liquid electrolyte in contact with the lead wire. Experiments show that the potential then increases in the case of $Pb\text{-}PbCl_2$ electrodes.

The electric resistance strongly increases during this dehydration, however as the amplifier which receives the signal of the electrodes has a very high input impedance, the measurement of this signal is not affected as long as the electrode resistance is not too large (about <100 kΩ).

5.3 Mitigation of the Dehydration Process

Experiments on hygroscopicity of salts in saturated solutions with additional non-dissolved salt (CLERC et al., 1998) demonstrate that there exists an equilibrium state (no evaporation and no absorption of the air humidity) which depends on the relative humidity (RH) of the air, the nature of the salt and the temperature. For

example, at 25°C this equilibrium is reached for 88% RH for KCl and 82% RH for NaCl. Therefore NaCl keeps its water in a lightly dryer atmosphere and is then slightly more hygroscopic than KCl.

Even for a dry near-surface ground, the relative humidity of the air remains (except for very particular cases) quite important at depth. To reduce the dehydration, the electrodes must be grounded deep enough (if possible) to generate a relative humidity larger than the equilibrium value and, as seen above, it is preferable to use NaCl electrodes. We note that the small cross-section channel used to limit salt exchanges is also useful to delay the dehydration of the electrode. The electrode must be placed in salted clay mud in order to guarantee a good contact with the ground. The mud volume to be used varies from about a litre for damp ground to tens of litres for dry ground.

5.4 Electrodes in Damp Ground

On the contrary, if the ground is damp or saturated in water, diffusion of ions between the electrodes and the ground tends to equilibrate the concentrations of the two media, and consequently to decrease the concentration in the electrode. As long as the non-dissolved salt exists, the solution remains saturated and the potential is kept constant. The study of this diffusion between two media at different concentrations allows us to determine the time span during which the potential remains constant, and to look for the conditions to increase this time span.

5.5 Study of the Diffusion

a. Cylindrical electrode. The general phenomenon of diffusion is described, in the case of diffusion of molecules or ions in solutions, by the first law of Fick:

$$dm/dt = -kS \, dC/dt \qquad (16)$$

m mass of dissolved salt
S cross section of the electrode
k diffusion coefficient
C concentration of dissolved salt
t time.

Initially, we assume a linear variation of the concentration from the outside of the electrode to the front of dissaturation (Fig. 6). The different concentrations are expressed in terms of the saturation concentration:

C_S concentration at saturation ($C_S = 1$)
C_M maximum concentration ($C_M > 1$ with non-dissolved salt)
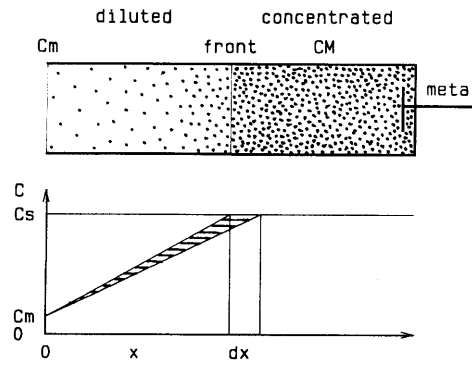C_m minimum concentration outside the electrode.

Figure 6
Diffusion in cylindrical electrode.

The front of dissaturation proceeds by dx during time dt. The corresponding salt mass variation is the sum of two terms: the first one, illustrated by the hatching triangle of Figure 6, results from the linear variation of concentration; the second is the mass coming from the non-dissolved salt in the volume $S\,dx$:

$$dm = -(C_S - C_m)\,dx/2 - (C_M - C_S)\,dx \quad \text{or} \quad dm = -(2C_M - C_S - C_m)\,dx/2. \tag{17}$$

The expression of dm is negative because m has decreased in the volume under study and m has been eliminated through the section at $x = 0$. Applying the Fick's law (16) with $dc/dt = (C_S - C_m)/x$, we obtain:

$$-2S\,dm/dt = (2C_M - C_S - C_m)\,dx/dt = 2k(C_S - C_m)/x. \tag{18}$$

Finally integrating from $x = 0$ to $x = L$ (L distance from the metal to the outside of the electrode), the time of dissaturation (t_D) is:

$$t_D = \frac{(2C_M - C_S - C_m)}{(C_S - C_m)}\frac{L^2}{4k}. \tag{19a}$$

The time of dissaturation is proportional to the square of the electrode length. In the absence of additional non-dissolved salt ($C_M = C_S$), t_D becomes independent of the concentrations:

$$t_D = L^2/4k. \tag{19b}$$

We have the same result if the concentration in the electrode varies from C_S to C_m because dm and dC/dx decrease proportionally to each other. Finally, if the concentration in the electrode is equal to the external concentration, the formula (19a) is indeterminate, the system is in equilibrium, and there is no more diffusion.

As in fact the front of dissaturation slowly proceeds with time, the variation of concentration is not exactly linear in x. A more detailed study reveals that the curve

is slightly convex upwards, which increases the slope near the outside of the electrode and decreases it near the front of dissaturation.

We look for a solution by numerical computation and a trial and error technique. First, we represent the concentration in the function of x by:

$$C = C_m + (C_S - C_m)[(x/x_1) + F] \tag{20}$$

where x_1 is the abscissa of the front of dissaturation and F is a corrective term added to a linear variation. The constraints are the following: $C = C_m$ for $x = 0$ and $C = C_S$ for $x = x_1$. This implies $F = 0$ for $x = 0$ and $x = 1$. Second, we look for an expression of F such that the Fick's law is verified in the whole interval from $x = 0$ to $x = x_1$ (x_1 abscise of the dissaturation front). It results that the variation in x is well fitted by a third degree polynomial. Consequently, for dimensional reasons, $(k.t)^{1.5}$ is introduced into the denominator. We must also express the variation of F in function of concentrations, which we will do through a term G_F, whence:

$$F = G_F(x\, x_1^2 - x^3)/(K\, t)^{1.5}. \tag{21}$$

It has been determined that the following form of G_F provides a good representation:

$$G_F = 0.034(2.2 C_M^{0.7} - 1.2 C_M^{-0.7} - C_S)/(C_S - C_m). \tag{22}$$

When the front of dissaturation reaches the metal wire ($x_1 = L$), t is t_D, the dissaturation time. T_D is *a priori* written in the form:

$$t_D = G_T L^2/k \tag{23a}$$

and our search method produces for G_T, which represents the variation of t_D in function of concentrations, the expression:

$$G_T = 0.082(25 C_M^{1.72} - 24 C_M - C_S)^{0.58}/(C_S - C_m). \tag{23b}$$

Example: Mud with KCl, $C_M = 2$ (2 saturations, i.e., 2×355 g/l) $k = 8.6 \times 10^{-10}$ m²/s or 74.4 mm²/day and external concentration $C_m = 0$

$$t_D = 0.0084\, L^2.$$
$$\text{day} \qquad \text{mm}$$

For a saturated medium without additional non-dissolved salts ($C_M = C_S = 1$), T_D is zero. Let us notice that this is not the case with the approximate formula (19a). Therefore, without additional non-dissolved salts, the electrode potential changes instantaneously as soon as the electrode makes contact with an external medium at a weaker concentration. However, if the electrode is long enough or provided with a narrow channel, the variation of the potential is slow.

Therefore, a formula (19a) gives dissaturation time values too large when C_M is weak. For $C_M = 3$, the difference between the results of (19a) and (23a) is still one

of 10%. For C_M larger the variation of the concentration as a function of x takes a linear trend, and the two expressions give identical values. Nonetheless, for the standard concentrations ($C_M < 3$), formula (23a) must be used.

b. *Electrode with a channel.* Figure 7 displays the sketch of an electrode with a channel. L and l are the lengths of the electrode body and channel; S and s are the cross sections of the electrode body and channel, respectively. We can study the very interesting case when $s \ll S$ and the dissaturation is strongly limited by the channel. At the junction between the channel and the electrode body, the concentration is close to saturation. The flow dm/dt in the channel is $Q_C = ks(C_S - C_m)/1$.

The dissaturation time is the ratio of the mass of available salt in the electrode body (beyond saturation) to the flow in the channel:

$$t_D \approx \frac{(C_M - C_S)}{(C_S - C_m)} \frac{SLl}{k_s}. \tag{24}$$

As SL is the volume of the body and $l/s = R/\rho$ (R is the electrode resistance, which depends mainly on the channel resistance, and ρ is the resistivity), it follows:

$$t_D \approx \frac{(C_M - C_S)}{(C_S - C_m)} \frac{VR}{k\rho} \tag{25}$$

i.e.,

$$t_D = A\ VR.$$

We conclude that the dissaturation time linearly depends on: 1) the store of salt, 2) the electrode volume, 3) the internal resistance.

Let us note that the ions diffusion and the electrolyte conductance are linked to the ions mobility; it is then logical to obtain T_D proportional to R. In formula (25) the product $k\rho$ is constant and R only varies with the channel size and the nature of the used internal medium.
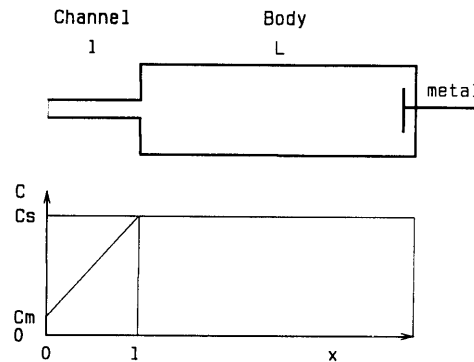

Figure 7
Diffusion in electrode with channel.

5.6 Diffusion Coefficients and Resistivity

The clay mud allows the time of dissaturation to increase by 1.9 relative to the liquid electrolyte along; and, using NaCl, we win a factor 1.5 relative to KCl. Our measurements lead to the following diffusion coefficients and resistivities:

k liquid	KCl	1.6×10^{-9}	NaCl	1.09×10^{-9}	m^2/s
–	–	138	–	94.2	mm^2/day
k mud	KCl	8.6×10^{-10}	NaCl	5.86×10^{-10}	m^2/s
–	–	74.4	–	50.6	mm^2/day
ρ mud	KCl	0.088	NaCl	0.129	Ωm

5.7 Numerical Applications and Verifications

Let us consider clay mud with KCl, $C_M = 2$ (2 saturations, i.e., 2×355 g/l) $k = 74.4$ mm^2/day, $\rho = 88$ Ωmm, $C_m = 0$ (t_D minimum). Then

Electrode without channel	Electrode with channel
(23a)	(25)
$t_D = 0.0084\ L^2$	$t_D = 1.2 \times 10^{-4}\ LD^2\ R$
day mm	day mm Ω

Application to four electrodes of the identical volume:

	Electrode without channel		Electrode with channel	
L (mm)	50	150	150	150
D (mm)	47	27	27	27
R (Ω)	5	30	500	1000
t_D	21 days	6.3 months	18 years	36 years

With a more important quantity of non-dissolved salt ($C_M > 2$), the dissaturation time is strongly increased. However, experiments on electrodes without channel show that, from $C_M = 5$ the increase is smaller than the calculated ones, and a maximum is reached for $C_M = 8$. The change of the mud structure with the salt dissolution is certainly one of the causes of this discrepancy, because the mud then tends to become a liquid electrolyte. We point out that lead chloride must not dissaturate either. But with a concentration of 40 g/l (4 saturations, $C_M = 4$) this dissaturation is not of vital concern.

Our dissaturation formulae have been verified in the laboratory by numerous experiments in which we varied the length of the cylindrical electrodes, the dimensions of the electrodes with a channel, and the concentrations (C_M). The electrodes we used had small dimensions in order to accomplish reasonable

dissaturation times, from a few hours to a few months. Setting the base of the electrodes into water and measuring regularly the potential to detect its increase at the moment of dissaturation made the measurements. Other experiments have been conducted in the ground for dissaturation times spanning a few months to two years. With variable ground conditions (for example damp but non-saturated) measured values are sometimes larger than the calculated ones by 20 to 40%.

We have noted in the introduction that some ions, different from those used in the electrode, can modify its potential. When these ions are present in the soil, they enter the electrode and its potential is perturbed. This perturbation can take place long before the dissaturation time calculated above, because the buffer effect of a saturated solution with additional non-dissolved salt does not exist. Of course the risk of perturbation depends on the soil composition. The channel is useful again to reduce the ions entry in the electrode.

5.8 *Comparison with Other Solutions*

One may also use electrodes with a reserve of liquid electrolyte as LESMES (1998) or SCHWARZ (1998). A slight flow through the porous ceramic is obtained owing to an air inlet in the electrode. Therefore the internal concentration remains constant, and furthermore this flow may improve the contact in a dry ground. As there is consumption of electrolyte, a reservoir or a filling system is necessary, which complicates the installation. It is difficult to maintain a regular flow, and surveillance and interventions are necessary. On the other hand, if the ground is soaked, water can enter the electrode (this process is different from diffusion) and quickly perturbs its potential.

Without air inlet and with a weakly porous material contact, no flow occurs and, in a damp ground, diffusion intervenes. For example, the electrodes built by JUNGE (1990) are composed of a FILLOUX's (1987) Ag-AgCl electrode placed in a chamber filled with a saturated KCl solution with additional non-dissolved salt. The ceramic has the same effect as the channel described above, in addition to ensuring contact with the ground. As the concentration gradient is mainly located through this porous ceramic, in HEMPFLING's (1977) electrodes with three chambers, the effect of three walls amounts to a slowdown of the dissaturation of the internal part. The dissaturation time of this type of electrodes is therefore expected to be proportional to the electrical resistance of the porous parts and to the quantity of the additional non-dissolved salt.

BOGORODSKY and BOGORODSKY (1995) describes an interesting device (that he has used for a number of years). A Pb-PbCl$_2$ electrode (useful length ~ 8 cm) is placed at the bottom of a plastic vessel, 20- to 30-cm high, filled with a mud made of soil to which considerable salt has been added (NaCl). The whole is equivalent to a very big electrode, containing substantial non-dissolved salt, and for which the distance between the electrode metal and the ground (the top of the vessel) is 30–40 cm. This allows obtaining a dissaturation time (formula (19a)) of several years.

The same advantage is obtained by MEUNIER (1995) using a Cu-CuSO$_4$ electrode with the electrolyte fixed in clay. The combination of three cylindrical vessels placed upside down, allows him to increase the current distance between the metal and the outside of the electrode. With an external diameter of about 9 cm and a height of 30 cm, a dissaturation time exceeding one year is expected by the author (and is certainly considerably larger in reality).

Our solution with a channel allows us to obtain a very important dissaturation time with an electrode of small volume (example $\varnothing$ 32, L 180 mm) and a quite acceptable internal resistance ($< 1000 \, \Omega$). A porous plug placed behind the channel (Fig. 8) ensures a good contact with the ground. The two functions, limitation of the dissaturation and contact with the ground, are separated here. The low volume of these electrodes permits an easy set-up after which no particular maintenance is necessary.

6. Fabrication of the Electrodes

A sketch of electrodes planned for long-time measurements is given in Figure 8. The composition of the clay mud is:

Water	HCl conc (33%)	KCl (or NaCl)	PbCl$_2$	Clay or Kaolin
1 litre	3.7 cm^3	680 g 720 g	40 g	1.65 kg

Salts, clay or kaolin must be in powder. A purity of 99% for salts is sufficient. It must be noted that lead electrodes are very weakly sensitive to impurities, but that such is not the case, for example, for silver electrodes.

The mud must be prepared a few days in advance; after these few days the dose of acid can be adjusted to obtain a pH of 4 to 5. The lead wire used ($L = 85$ mm, $\Phi = 1.6$ mm) is a standard one. Numerous experiments show that a high purity or a larger size of the wire does not create better results. Nevertheless, the wire must be carefully cleaned with tissues impregnated with a solvent such as trichloroethylene or acetone.

The electrode is filled with mud. The piece through which the channel is pierced must be correctly fitted on the tube to avoid leakage. With a 10-mm long channel and a 1.7-mm diameter, the internal electrical resistance of the electrode is 400 Ω with KCl, and the calculated dissaturation time is about 14 years. Finally, the electrode is closed by a porous plug: glued ceramic or wood simply maintained by its natural expansion with moisture.

After manufacturing, the electrodes are stored in a box on a bed of plastic foam soaked with a saturated KCl or NaCl solution (same salt as in the electrodes). Their potential is measured every day over one or two weeks with respect to a reference electrode. This reference can be one electrode of the current set or, better, an older electrode from a previous manufacturing. The scattering of potential values is (except for accident) smaller than or equal to 0.2 mV.
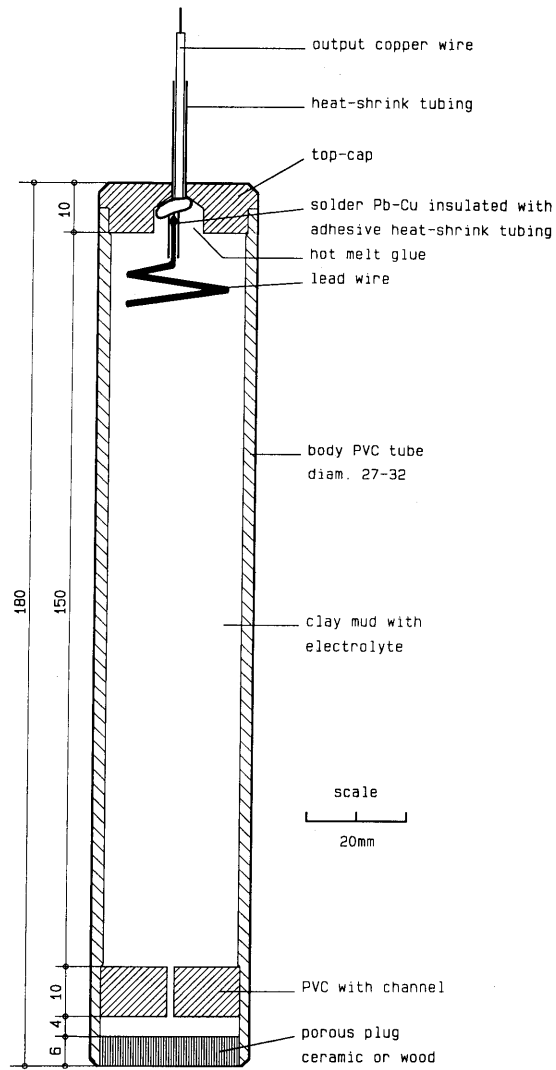
Figure 8
Electrode for long-term measurements.

Let us note that the "tube" electrode model described in 1980, easy to set up and recover, is always valid for measurements continuing a few hours to a day, with the following modifications: plaster is to be replaced by mud and lead wire must be located at the top of the part filled with mud. Wood is the best solution for the porous plug. The channel is not necessary for these short duration measurements.

7. Conclusion

The variation of the electrode potential as a function of the concentration of $PbCl_2$ and KCl 1) has experimentally been determined; 2) has permitted to derive a calculation method of this potential; 3) has permitted to show that the chemical equilibrium of the Pb-$PbCl_2$ electrodes is due to the formation of a complex formed of Pb^{++} and Cl^- ions.

With an internal pH adjusted to 4 or 5, the stability of the potential is improved and the noise decreased for KCl electrodes as NaCl electrodes.

The main advantage of the KCl electrodes is a very small temperature coefficient. In the ground however, it resists dehydration less well than NaCl electrodes do. Furthermore, KCl is a high quality food for plants. The presence of KCl in the ground, at weak concentrations at the edge of the electrodes, favours the growth of roots and the local potential can be disturbed (PERRIER et al., 1997). As a consequence, if the electrodes are grounded at sufficient depths (about 1 m), the temperature variations are very weak; it is preferable to use NaCl electrodes.

The study of the salts diffusion has permitted to establish formulae for the calculation of the dissaturation time. With a saturated electrolyte and additional non-dissolved salts, stabilised in a thick clay mud and using a channel of small section to limit exchanges with the outside, the dissaturation time can be considerably larger than ten years.

Our electrodes have a weak volume, are insensitive to the orientation and therefore easy to set up. Afterwards they work maintenance-free. For example, these electrodes are successfully used in various geophysical domains: volcano survey (ZLOTNICKI and LE MOUËL, 1988), study of the long-term telluric variation on a site (PERRIER et al., 1998), search of telluric signals related to earthquakes (GRUSZOW, 1997), determination of the upper mantle resistivity (LEMONNIER et al., 1998) or magnetotelluric measurements (see FILLOUX et al., 1994).

Finally, the realisation of the electrodes can be adapted to the short duration of measurements (magnetotelluric, reference electrodes in laboratory). As diffusion takes place only during the time of measurements, it is very weak. When the electrodes are not in service they are stocked on foam soaked with a solution of the same composition as the internal electrolyte in order to prevent diffusion. For this short time utilisation of the electrode volume can be considerably reduced.

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