

Electrochemical fundamentals of self-potential anomalies and their application to the situation of the KTB

1. Introduction

Self-potential (SP) anomalies, i.e. minima of the electrical potential field at the earth's surface being nearly constant in time, are well known geophysical phenomena [1]-[3],[7]. These minima amounting up to -1.8 V and extending over some hundred meters are associated with ore and/or graphite deposits in the depth.

According to the theory by Sato and Mooney [1], the anomalous course of the electrical potential at the earth's surface is caused by electrochemical reactions in the upper earth mantle. An electronically conducting material (e.g. graphite) connects oxidizing zones close to the earth's surface with reducing zones at some depth. Both the electronic conductor and the electrolytically conducting rock environment represent a kind of giant electrochemical cell (geobattery). The iR drop due to the ionic current flowing along the earth's surface manifests itself as SP anomaly (fig. 1a).

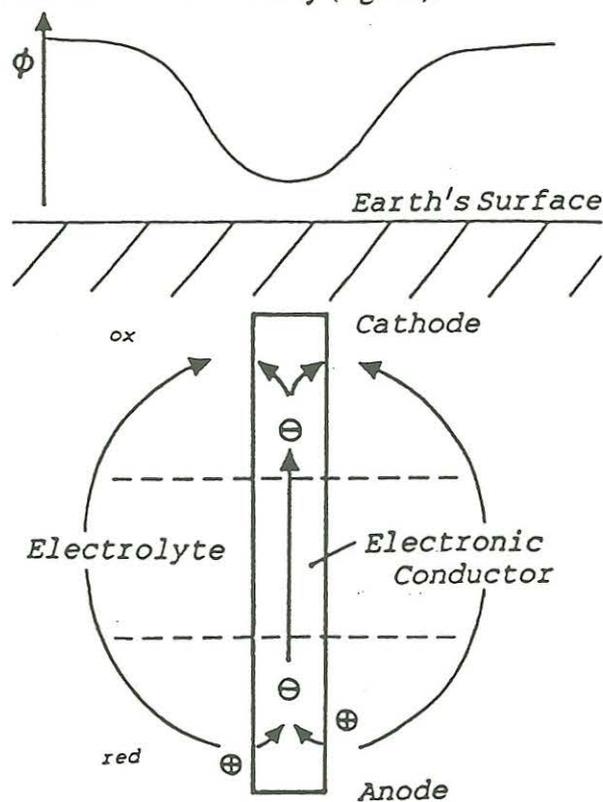


Fig. 1a: Origin of a SP anomaly (ϕ : electrical potential).

In the immediate vicinity of the Continental Deep Drilling (Kontinentale Tiefbohrung KTB) in the Oberpfalz (Bavaria) a SP anomaly has been observed amounting to -0.6 V [7] (fig. 1b). The drilling hole offers the unique possibility to obtain important parameters for modeling the SP anomaly near the KTB drilling hole and to get a more extensive understanding of SP anomalies. In cooperation with the Institute of Geophysics (Frankfurt University) it is intended to clarify the origin of the SP anomaly near the KTB by utilizing measurements of various parameters (electrical potential, redox potential) within the drilling hole [8].

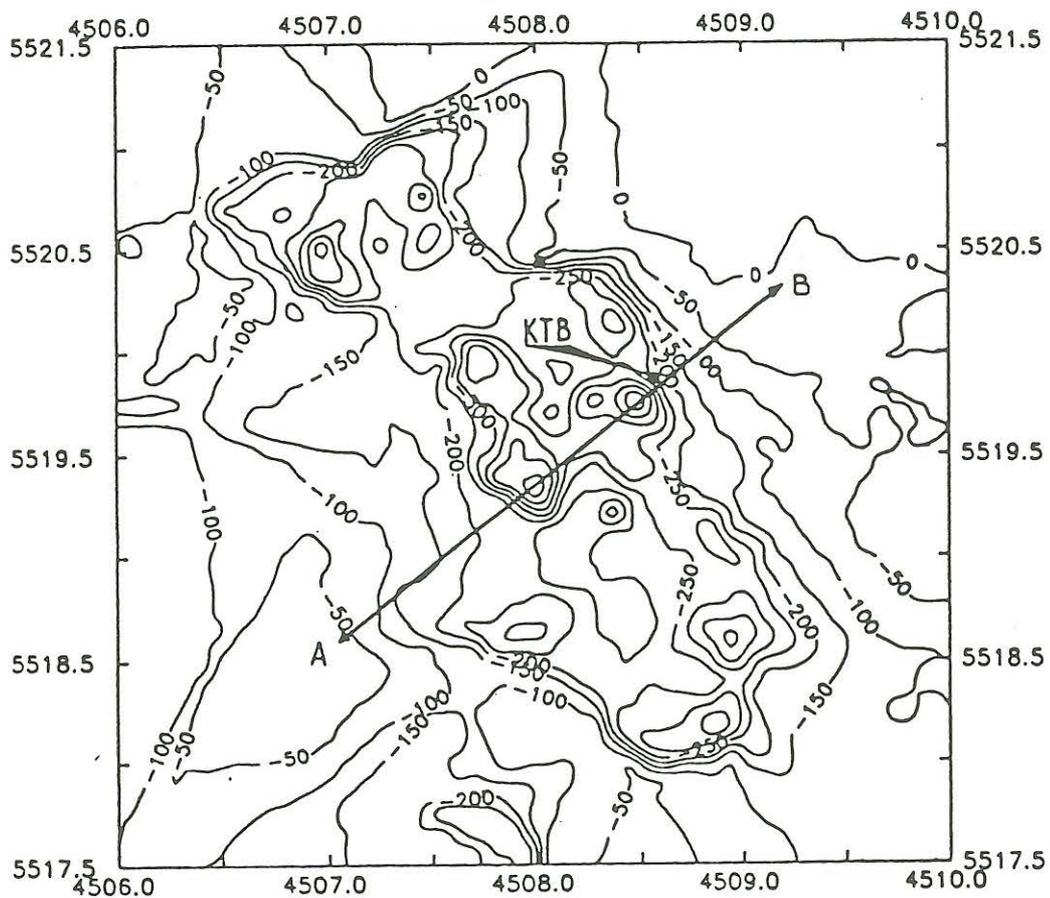


Fig. 1b: SP anomaly at the KTB environs [7].

This paper deals with the calculation of self-potential anomalies which are caused by geobatteries. In order to develop an adequate algorithm for calculating of geobatteries, laboratory simulations were made with synthetic materials accounting for the redox potential field (E_R), the position of the electronic conductor, and kinetic parameters of the reactions taking place at the anode and cathode of the cell.

2 Laboratory experiments

In a first approach the SP anomaly is modeled by a simple two-dimensional paper cell (fig. 2) which is drenched by an electrolyte and to which a redox gradient is applied. A strip of platinum representing the electronic conductor links the regions of different redox potential E_R . The electrical field E_F of the cell is measured by using two reference electrodes, one of which being scanned over the paper. A data collecting system serves for automatically measuring and numerically handling of the data.

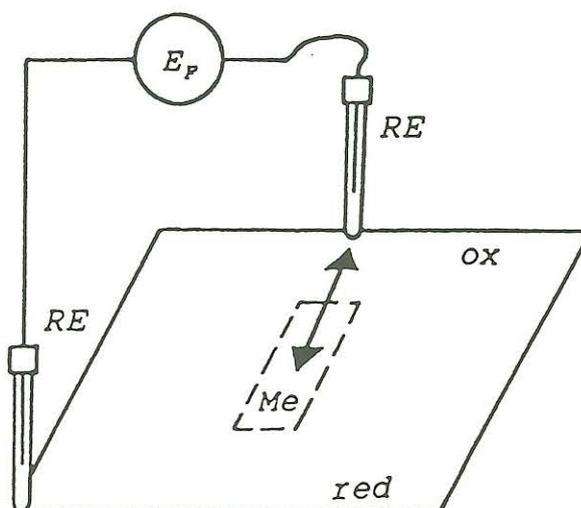


Fig. 2: Simulation of a SP anomaly using a paper cell. RE: Ag/AgCl reference electrodes; Me: metal strip of platinum; ox: $\text{Fe}_2(\text{SO}_4)_3$; red: FeSO_4 ; E_F : electrical potential.

3 Results of laboratory experiments

The geometrical relationship between the redox potential field E_R and the electronic conducting material decisively controls the course of the resulting electric field E_F . Fig. 3 illustrates the course of the potential field generated by different distributions of the redoxactive species which determine the extension of the anode and cathode of the battery. If the oxidation zone (Fe^{3+}) and the reduction zone (Fe^{2+}) are distributed symmetrically with respect to the electronic conductor the potential difference at the surface ($z=0$) is just about half of the cell potential defined by the potential difference between anode and cathode (fig. 3a). If however the oxidation zone is small compared with the reducing zone (fig. 3 b), the potential difference at the surface is much larger than half of the cell potential.

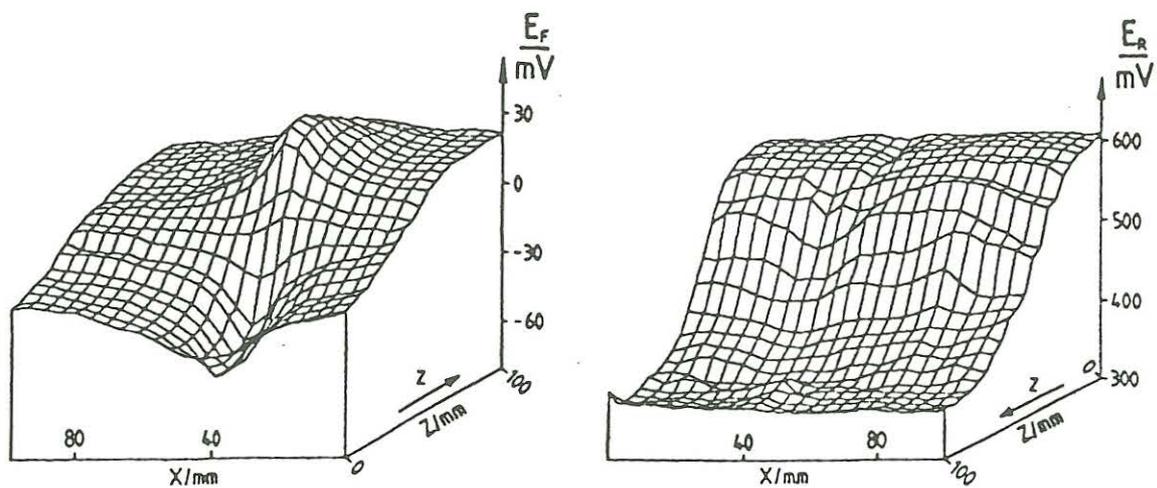


Fig. 3a: The course of the potential field E_F generated by a symmetrical distribution of the redox species and, correspondingly, of the redox potential E_R .

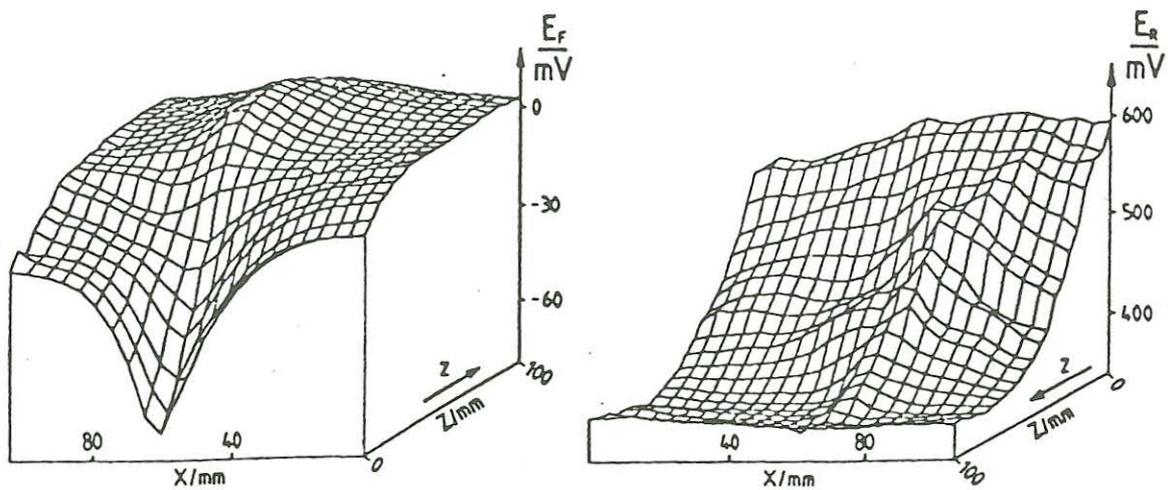


Fig. 3b: The course of the potential field E_F generated by an asymmetrical distribution of the redox species and of the redox potential E_R .

On the basis of the paper cell an algorithm for calculating the potential field is developed taking in account the redox gradient as well as the kinetic and transport processes dependent on their location on the electronic conductor.

4 Development of an algorithm for calculating geobatteries

4.1 Electrochemical fundamentals

If an inert electrode (e.g. platinum) dips into an electrolyte solution containing a redox couple, the species which is transferred between the two phases 1 (metal) and 2 (electrolyte) are electrons. The electrochemical potential $\bar{\mu}$ of the electrons in either phase is the sum of the chemical potential μ and the electrical energy $z F \phi$:

$$\bar{\mu} = \mu + z \cdot F \cdot \phi, \quad (1)$$

where z is the (signed) charge number of the species (for electrons: $z=-1$), F is the Faraday constant, and ϕ is the electrical potential. At equilibrium the electrochemical potentials of the electrons in both phases 1 and 2 are equal. From

$$\bar{\mu}_1 = \bar{\mu}_2 \quad (2)$$

or

$$\mu_1 + z \cdot F \phi_1 = \mu_2 + z \cdot F \cdot \phi_2 \quad (3)$$

follows

$$\Delta\phi^\circ = \phi_1 - \phi_2 = \frac{1}{z \cdot F} (\mu_2 - \mu_1). \quad (4)$$

This means that an electrical potential difference $\Delta\phi^\circ$ (Galvani voltage) arises between the two phases. The Galvani voltage $\Delta\phi^\circ$ can not be measured directly. It can be measured - by neglecting diffusion effects - with respect to the Galvani potential $\Delta\phi_H$ of a standard hydrogen electrode as a reference. Since $\Delta\phi_H$ is constant under standard conditions of pressure, temperature and pH, the potential difference $\Delta\phi^\circ - \Delta\phi_H$ is a function only of the kind and concentration of the redoxactive species within the electrolyte. For the standard condition of 1 mol/dm^3 redox species concentration (assuming ideal behaviour) the potential difference $E^\circ = \Delta\phi^\circ - \Delta\phi_H$ is called the standard potential.

For any concentration of the redox species the potential difference $\Delta\phi^\circ - \Delta\phi_H$ is called redox potential E_H . When a Ag/AgCl reference electrode is used instead of the standard hydrogen electrode, the difference $E_R = \Delta\phi^\circ - \Delta\phi_{Ag/AgCl}$ is shifted by a constant value of approximately 200 mV with respect to E_H . A high redox potential is equivalent to a low chemical potential of the electrons in the electrolyte phase. This means that the electrolyte

phase tends to accept electrons. In contrast, an electrolyte phase with a low redox potential indicates that the electrolyte phase tends to spend electrons.

If an inert electronic conductor connects regions of different redox potential E_R^1 and E_R^2 (e.g. graphite within the earth's crust), it must have a potential E_m between E_R^1 and E_R^2 (fig. 5). This is a very important fact for understanding SP anomalies. Assuming the reaction kinetics to be infinitely fast, the electrochemical potential of the electrons within the electrolyte near the conductor is constant, namely equal to the electrochemical potential of the electrons within the electronic conductor. This results from the fact that *not* the electrical but the electrochemical potential forms equipotential lines along the electronic conductor. In reality - because of a finite rate constant of the reactions taking place at the anode and cathode of the conductor - a small difference of the electrochemical potential at the interface between the two phases (conductor/electrolyte) will remain (c.f. 4.2). This difference is proportional to the so-called overpotential.

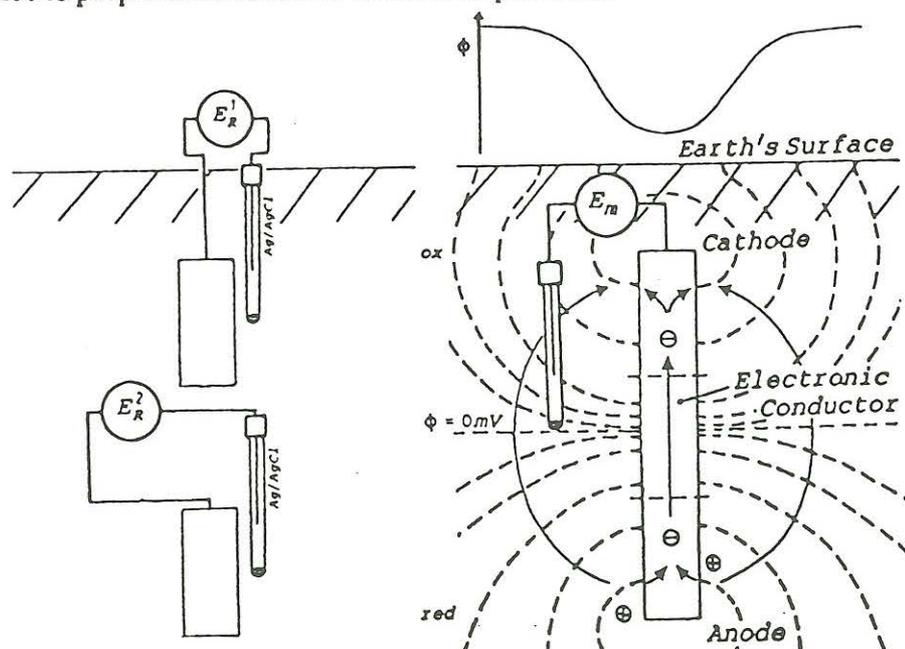


Fig. 5: The potential E_m of an inert electronic conductor in a medium of different redox potential E_R^1 and E_R^2 . (a): electrodes are isolated, (b): electrodes are interconnected (battery short-circuited).

4.2 Formulation of the algorithm

Since the generation of a SP anomaly occurs under nonequilibrium conditions, the ohmic potential drop iR in the electrolyte surrounding the electronic conductor and

involving diffusion and migration processes exists as long as the geobattery works. In addition, the charge transfer kinetics is by far not infinitely fast. Hence for describing a geobattery it is absolutely necessary that kinetic parameters such as the current exchange density must be accounted for. For such a mathematical description of a geobattery one starts with the Ohmic law

$$\vec{j} = -\sigma \cdot \text{grad} \phi, \quad (5)$$

where \vec{j} is the ionic current density (in A/m²), σ is the ionic conductivity of the rock (in S/m) and ϕ is the electrical potential (in V). The resistivity of the electronically conducting material is assumed to be negligible compared with that of the electrolytically conducting rock environment. The first derivation of equation (5) yields

$$\text{div} \vec{j} = -\text{grad} \sigma \cdot \text{grad} \phi - \text{div} \text{grad} \phi. \quad (6)$$

For simplicity the ionic conductivity σ is taken as a scalar function depending only on the location within the earth's crust. If σ is constant in space, equation (6) reduces to the Poisson equation. The source density $\text{div} \vec{j}$ having the dimension A/m³ or C/(s·m³) represents the rate of charge production per unit volume. It equals to zero everywhere in the system except at the interface between electrolyte and electronic conductor. For calculation of the source density $\text{div} \vec{j}$, electrochemical considerations are introduced: the current density j flowing perpendicularly through the interface electrolyte/electronic conductor depends on the difference of the electrochemical potential of electrons between these two phases, which is proportional to the overpotential η as shown by the following calculation ($z=-1$):

$$\frac{1}{F}(\bar{\mu}_2 - \bar{\mu}_1) = \frac{1}{F}(\mu_2 - F \cdot \phi_2 - \mu_1 + F \cdot \phi_1) = (\phi_1 - \phi_2) - \frac{1}{F}(\mu_1 - \mu_2). \quad (7)$$

Using eq. (4) with $z = -1$ it follows

$$\frac{1}{F}(\bar{\mu}_2 - \bar{\mu}_1) = \Delta\phi - \Delta\phi^\circ = \eta. \quad (8)$$

Eq. (8) represents the definition of the overpotential: the difference between the actual Galvani voltage $\Delta\phi$ at flowing current and that at equilibrium $\Delta\phi^\circ$. The net current density j flowing across the conductor/electrolyte interface is related to the exchange

current density j_0 at equilibrium and the overpotential η by the Butler-Volmer equation:

$$j(\eta) = j_0 \left\{ \exp\left(\alpha \frac{n \cdot F}{R \cdot T} \eta\right) - \exp\left((\alpha - 1) \frac{n \cdot F}{R \cdot T} \eta\right) \right\}, \quad (9)$$

where n is the number of transferred charges, α is the transfer coefficient being related to the symmetry of the j -versus- η relationship for either direction of the charge transfer reaction, and R, T and F have the usual meaning. Because of the low current densities occurring on natural geobatteries, the overpotential is assumed to be small (but not negligible). Therefore the Butler-Volmer equation can be expanded into a Taylor series. Breaking off the series after the first member yields

$$j(\eta) = j_0 \frac{n \cdot F}{R \cdot T} \eta. \quad (10)$$

According to eq. (8) the overpotential η is given by the difference

$$\eta = \frac{\bar{\mu}_E - \bar{\mu}_m}{F}, \quad (11)$$

where $\bar{\mu}_m$ is the electrochemical potential of the electronic conductor and $\bar{\mu}_E$ is that of the electrolyte. The electrochemical potentials are given by

$$\begin{aligned} \bar{\mu}_E &= \mu_E - F(\phi_E + \phi) \\ \bar{\mu}_m &= \mu_m - F\phi_m \end{aligned} \quad (12)$$

where ϕ_E is the potential of the electrolyte at infinite distance from the geobattery and ϕ is the potential of the electrolyte at any position within the rock environments, both referred to a reference electrode at infinity. If no current flows, ϕ is zero anywhere. The overpotential is obtained from eq. (11), by accounting for eq. (4) and by using the definition $\Delta\phi = \phi_m - \phi_E$

$$\eta = \frac{1}{F} \{ \mu_E - F(\phi_E + \phi) - (\mu_m - F\phi_m) \} = -\Delta\phi^\circ + \Delta\phi - \phi. \quad (13)$$

By adding $0 = \Delta\phi_{Ag/AgCl} - \Delta\phi_{Ag/AgCl}$ eq. (13) gives

$$\eta = -(\Delta\phi^\circ - \Delta\phi_{Ag/AgCl}) + (\Delta\phi - \Delta\phi_{Ag/AgCl}) - \phi = -E_R + E_m - \phi. \quad (14)$$

where $E_m = \Delta\phi - \Delta\phi_{Ag/AgCl}$ is the potential of the electronic conductor with respect to a Ag/AgCl electrode in a distance infinitely from the geobattery. Thus inserting eq. (14) into eq. (10) leads to the current density

$$j = -j_0 \frac{n \cdot F}{R \cdot T} (E_R - E_m + \phi) . \quad (15)$$

From eq. (15) the source density is obtained as follows. By using the Gaussian integral theorem, the integration of $div \vec{j}$ with respect to a small region R of space yields

$$\int_R div \vec{j} dV = \int_{(R)} \vec{j} \cdot d\vec{F} \quad (16)$$

where (R) is the surface of the region R. The right hand side of eq. (16) is equal to the integral of the current density j (see eq. (10)) over the electrode surface (E) within region R:

$$\int_{(R)} \vec{j} \cdot d\vec{F} = \int_{(E)} j \cdot dF \quad (17)$$

With the definitions

$$\int_R dV = V \quad \text{and} \quad \int_{(E)} dF = F \quad (18)$$

and assuming $div \vec{j}$ and j to be constant within R and over (E), eq. (16) turns over to

$$div \vec{j} \cdot V = j \cdot F \quad (19)$$

or

$$div \vec{j} = g \cdot j . \quad (20)$$

where g represents the electrode area per unit volume or the specific area of the electrode within any (at least infinitesimal small) region R of space. Because F is a function of the location, the same is true of the quotient $g = F/V$.

Inserting eq. (15) into (20) and accounting for eq. (6) yields

$$div \vec{j} = g \cdot j_0 \frac{n \cdot F}{R \cdot T} (E_R - E_m + \phi) = grad \sigma \cdot grad \phi + \sigma div grad \phi . \quad (21)$$

This differential equation is used in the following calculations of the potential field in the paper cell as well as of a natural geobattery.

4.3 Results of calculations of the potential field in the paper cell

Fig. 6 shows the result of numerical calculations (a) of the electric field for a specific configuration of the paper cell compared with that obtained from measurements within it (b). Input parameters for the computer program are the measured redox potential field, the conductivity of the drenched chromatography paper, the position and extension of the electronic conductor and the exchange current density which results from the redox reaction taking place at the electrodes of the cell. Furthermore, the conductivity variation of the electrolyte as induced by the current flowing through the cell has been accounted for. From the good agreement between the calculated and the measured data it is concluded that the algorithm used is suitable for calculating natural geobatteries too.

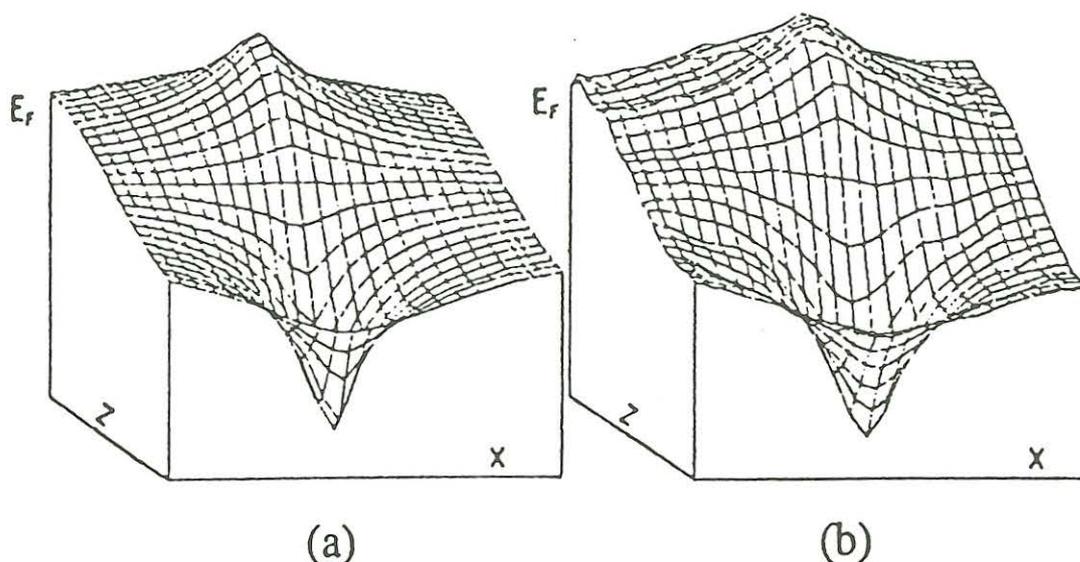


Fig. 6: Calculated (a) and measured (b) electrical potential E_F in the paper cell.

5 Calculation of the potential field of a natural geobattery

In the literature the redox potential of any redox system is usually presented with respect to the standard hydrogen electrode. Therefore, for the following calculations the redox potential E_H is used. In addition the following parameters are considered:

(1) The redox potential field E_H within the earth's crust which approximately varies as an exponentially decreasing function of depth [2],[3]:

$$E_H(z) = (E_H^s - E_H^d) \exp(-kz) + E_H^d \quad (22)$$

where E_H^s is the redox potential at the earth's surface, E_H^d is the redox potential at the depth and the penetration depth $1/k$ defines the zone of weathering. The E_H value of the weathering zone near the earth's surface amounts to 300..600 mV at pH 4..6 [3]. The E_H value in the depth can be derived from the existence of pyrite common with graphite (the inert conductor): since pyrite is thermodynamically stable the E_H value of the environment should be -400 to -150 mV at pH 7..8 as shown in fig. 7. The resulting E_H difference between surface and depth thus amounts to 450 up to 900 mV (fig. 7). For numerical calculations a penetration depth $1/k=150$ m is used.

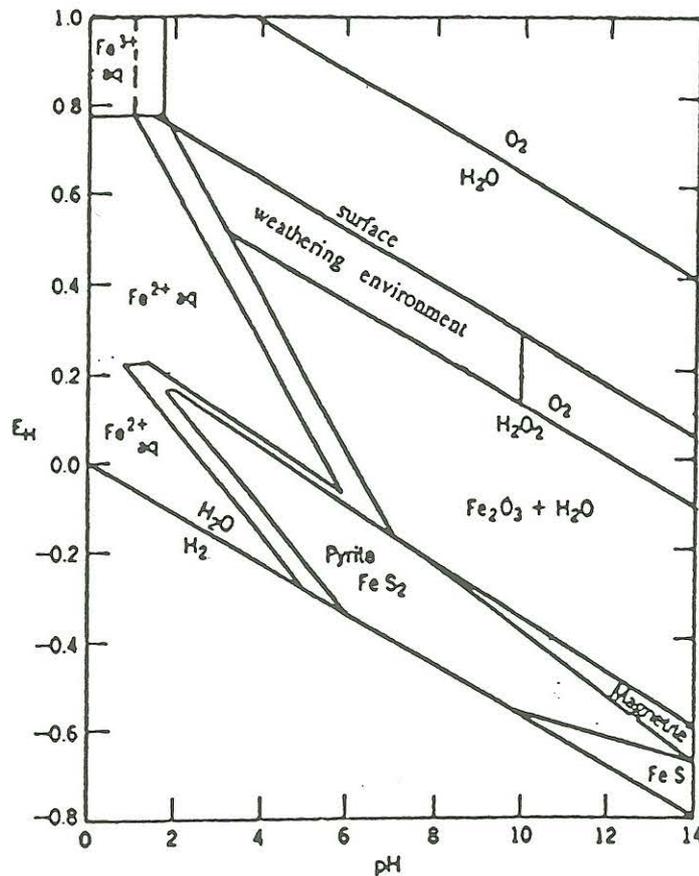


Fig. 7: E_H -pH diagram with respect to weathering zone and rock environment [2],[10].

(2) The resistivity of the rock environment can be taken from measurements in the vicinity of the KTB revealing values larger than 2000 Ωm [4]. This high resistivity rock material is

covered by a layer of 10 to 20 m thickness of low resistivity material (300..500 Ωm) [4],[5]. For the calculation the larger value of 2000 Ωm is used.

(3) The extension of the inert conductor is very uncertain. Within the KTB drilling hole, graphite was found at a depth of 1000 m and more. In principle, graphite may cover regions of several hundred meters up to kilometers. The dip of the electronic conductor, however, can be determined by the lithological correlation between the two drilling hole locations [6] and amounts to approximately $\alpha = 70^\circ$.

(4) Kinetic parameters are obtained by scaling up the paper cell to the dimensions of natural geobatteris. Thus the exchange current density is approximated by about 5 $\mu\text{A}/\text{m}^2$.

Fig. 7 shows the position of the electronic conductor near the KTB drilling location as assumed for the calculation of the SP anomaly.

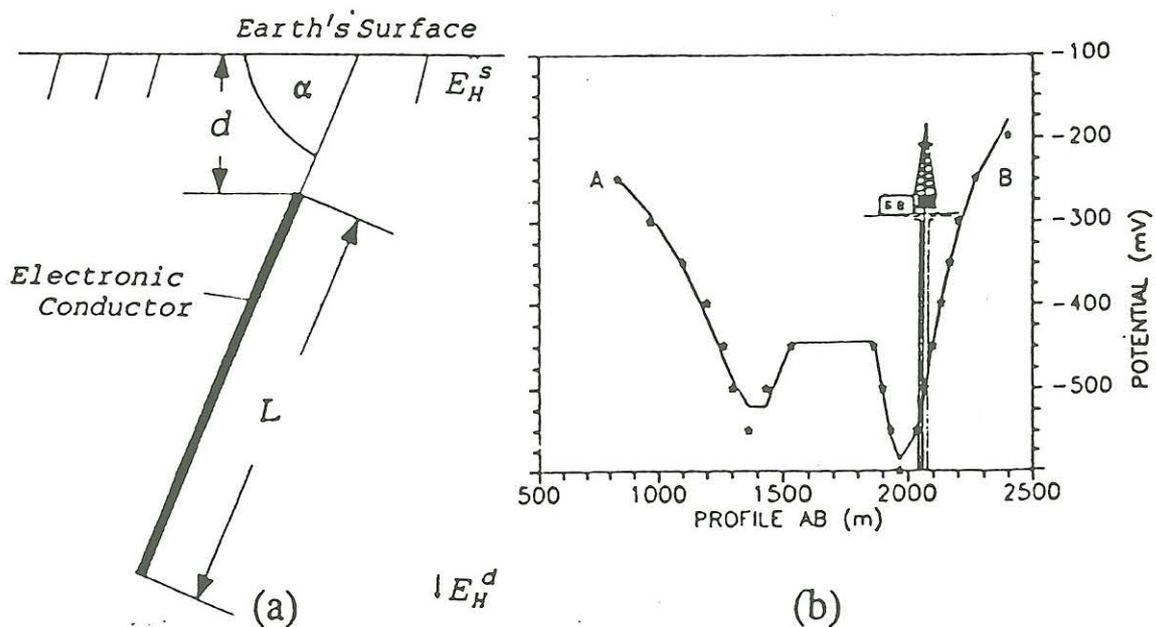


Fig. 7: (a) Position of the electronic conductor as modeled for SP calculations. (b) Course of the SP anomaly near the KTB obtained from measurements [7].

From the numerical calculations depicted in fig. 8 the following conclusions can be drawn:

- All bipoles are strongly unsymmetrical. In an extreme case, the potential difference measurable at the earth's surface, i.e. the SP anomaly approximately amounts to the maximum E_H difference (of 800 mV).

- The electronic conductor ends only some tens meters below the earth's surface.
- The electronically conducting material must at least range down to several hundred meters in order to produce a SP anomaly of -600 mV.

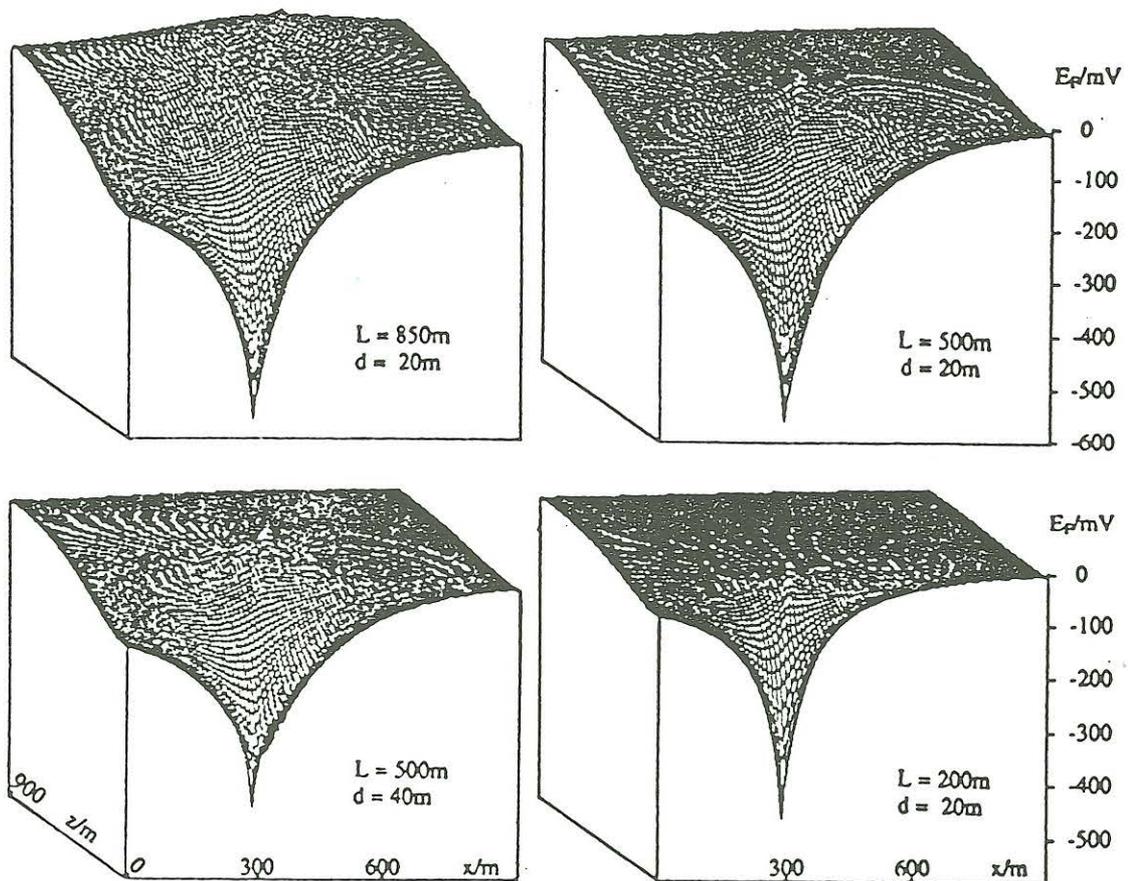


Fig. 8: Numerical modeling of the KTB SP anomaly. L is the length of the electronic conductor and d the distance between the earth's surface and the upper end of the electronic conductor (see fig. 7a).

6 Dimensional analysis and scale factors

For scaling-up of the paper cell to the dimensions of natural geobatteries, dimensionless parameters have to be introduced. The formulas for calculating of these parameters give a

hint at the significance of specific parameters of a geobattery (extension, specific conductivity of the rock environment, reaction kinetics) for the generation of high SP anomalies. These formulas can be obtained by similarity methods as well as by converting the differential equation (21) into a dimensionless form.

The latter has been performed by choosing characteristic parameters: length L (i.e. the length of the electronic conductor), maximum redox potential difference $E_{\max} = E_R(\text{surf}) - E_R(\text{depth})$ and maximum electrical potential difference ϕ_{\max} at the surface.

With the following substitutions

$$K = g \cdot j_0 \frac{n \cdot F}{R \cdot T}, \quad \left(\frac{d}{dx}\right)' = L \cdot \frac{d}{dx} \quad (23)$$

and with the normations

$$E_R' = E_R / E_{\max}, \quad E_m' = E_m / E_{\max}, \quad \phi' = \phi / \phi_{\max} \quad (24)$$

eq. (21) can be reformulated

$$E_R' - E_m' = a_0 \cdot \phi' + a_1 \cdot \text{grad}' \sigma \cdot \text{grad}' \phi' + a_0 \cdot B \cdot \text{div}' \text{grad}' \phi' \quad (25)$$

where

$$a_0 = \phi_{\max} / E_{\max}, \quad a_1 = \text{grad}' \sigma / (L^2 \cdot K) \quad \text{and} \quad B = \sigma / (L^2 \cdot K). \quad (26)$$

The question is: What do the equations (26) mean?

Assumed we have two batteries - a geobattery and its laboratory simulation - which are modeled numerically by eq. (21) or (25). In spite of the fact that the geometrical dimensions may be completely different, these two structures are called similar if their dimensionless parameters a_0 , a_1 and B are identical.

Let us focus on parameter B : Assumed σ and K are constant in space, the dimensionless parameter B (see eq. (26)) is also constant in space. For the paper cell B has a value of $2.7 \cdot 10^{-3}$, typically resulting from a characteristic length of $L=5$ cm, an average (two-dimensional) specific conductivity of 0.2 mS, and a kinetic parameter $K = 3$ mS/cm² obtained from j -versus- η measurements in the paper cell. Scaling-up of the paper cell to the dimensions of natural geobatteries by using $B=2.7 \cdot 10^{-3}$, $L = 100$ m, $\sigma^* = 1 \cdot 10^{-3} \Omega^{-1} \text{m}^{-1}$ results in $K=4 \cdot 10^{-2}$ mS/m³.

The dimensionless parameter β (see eq. (26)) thus signifies that the extension L of the electronic conductor is very important in relation to the electrode kinetics: a large geobattery does not need a large kinetic parameter K . This means that, while the reactions occurring at the electrodes may be slow, nevertheless a high SP anomaly can be generated.

7 Conclusions

(1) Potential measurements in a simple paper cell as a model of a geobattery and comparison with theoretical calculations indicate that the amplitude of a SP anomaly depends on the following parameters:

- difference of the redox potential between surface and depth
- distribution of the redox potential field
- position and extension of the electronic conductor
- electrochemical reaction kinetics

(2) Scale-up of the paper cell model and extension of the calculations to the natural geobattery of the KTB lead to the following interpretation of the SP anomaly:

- The electric field of the SP anomaly is extremely unsymmetrical.
- The extension into depth of the electronically conducting material amounts to at least several hundred meters.
- The electronic conductor ends approximately some tens meters below the earth's surface

As the amplitude of the SP anomaly does not depend on the amount of the graphite being present near the KTB, it may give quantitative information on the vertical gradient of the redox potential and the vertical extension of the electronic conductor.

(3) Electrochemical experiments in a high pressure - high temperature cell have to be performed and are in preparation in order to gain kinetic information on the electrode processes occurring under real conditions.

Acknowledgements

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