

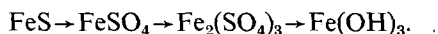
# INVESTIGATIONS ON THE ELECTRODE POTENTIAL OF SULFIDE ORES

MRS. M. AGÓCS

Institute of Mineralogy, Geochemistry and Petrography,  
Attila József University, Szeged

## INTRODUCTION

The main territory of weathering and sedimentation is the border between lithosphere and atmosphere characterized by the greatest change of the redox potential observed in nature. In the course of weathering mostly minerals containing elements with altering valency undergo changes, when their valency has not yet reached the highest one possible at redox values available in the nature [E. SZÁDECZKY-KARDOSS, 1952]. The weathering of sulfide ore deposits is especially remarkable, since the  $S^{2-}$  anion at the redox-potential-change observed on the surface changes into the central  $S^{6+}$  cation of the  $(SO_4)^{2-}$  complex anion. That is, sulfide ion on the surface changes into a sulfate with lower free energy, thus sulfide minerals change into sulfates of lower compound potentials. The ionic potential of sulfide ion is 1,16, that of the sulfate ion 0,68. This important fact is moreover supported by the role of cations with altering valence. The oxidation of sulfides containing cations with altering valency takes place in several steps. E.g. in the case of iron(II)-sulfide:



In the last step besides ferri hydroxide sulfuric acid is formed, what serves as a source for further reactions.

The rate of oxidation is influenced by other sulfides present since minerals with different chemical composition, different potentials, occurring simultaneously, after having got into contact with circulating mine water as electrolyte, form micro- and macro- galvanic elements, respectively. In consequence of this the weathering is not only a physical and chemical, but also an electrochemical process. Of two simultaneously precipitated sulfide ores the one having lower potential behaves like anode, i.e. oxygen separates on it, what accelerates the oxidation. E.g. in the case when marcasite and sphalerite get into contact, the electrode potential of which as related to copper is given by V. H. GOTTSCHALK and H. A. BUEHLER [1910] as 0,37 and —0,30, V., resp., sphalerite is oxidized 10—14 times more rapidly than alone.

Similar data for ores have been determined by H. RECHENBERG [1951] recalculating the obtained electrode potential values for normal hydrogen scale, to

compare them with the electrode potentials of the metals. On the basis of the obtained values RECHENBERG arranged the sulfide minerals into an electromotive force series, similar to that of the metals.

However, it was pointed out by GY. GRASSELLY [1954] that these two series cannot be considered as identical since in the case of ores it is impossible to suppose a uniform basis for comparison in respect to all of the deposits, thus it is impossible to write up a generally valid potential series, similar to metals. Namely in the case of ores it is not always solutions containing own ions that play the role of electrolytes and the ores cannot be regarded as reversible electrodes. On the other hand, the circulating mine water as electrolyte is not a solution with unit activity, thus the values measured are different from the normal redox potential value of metals in this respect, too. In view of these causes, it is impossible to give for the ores generally valid values of the normal redox potential, but the results obtained from a detailed study of the given mines and mineral associations, respectively, may be characteristic of the expected processes.

According to E. SZÁDECZKY-KARLOCS [1952] the oxidation of ores starts at a certain redox potential value as determined by the redox value necessary for sulfide sulfur to change into atomic sulfur. This redox value in  $10^{-2}$  mole dilution, at  $\text{pH}=0$ , is about  $+0,2$  Volt; at  $\text{pH} = 7$   $-0,2$  Volt. This supposition seems to be proved by GARRELS calculations as well [1954].

The weathering and sedimentation of sulfide ore deposits is a process having importance for geochemistry, since on the one hand it results in concentration of some important metallic elements in the oxidation zone itself, and in the underlying cementation zone on the other. Namely through an interaction of the unchanged sulfide ores with sulfate and sulfuric acid solutions, moving downwards, sulfides of relatively more noble metals and native metals respectively, may be precipitated and enriched.

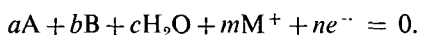
## THEORETICAL PART

Electrochemical processes resulting in weathering of sulfide ore deposits are essentially such oxidation-reduction processes in which both electron migration and changes in the hydrogen ion concentration play an important part. In the case of metals POURBAIX has dealt with the generally possible processes. He first used the redox potential — pH equilibrium diagrams (nowadays named after him), to characterize metal — water systems, to illustrate their dissolution and stability relations, respectively.

It was R. M. GARRELS [1954] who applied the POURBAIX-diagrams for the stability relations of natural systems in order to interpret processes taking place in the nature.

The superposition of POURBAIX-diagrams and the explanation of the behaviour of multicomponent systems was carried out the first time by J. HORVÁTH and M. NOVÁK [1964] drawn the diagrams of several metal-sulfur-water ternary systems from corresponding thermochemical data.

In order to secure a systematic method of interpretation the following conventions are assumed: any reaction in which substance A is converted into substance B can be written in a form where the equation, besides substances A and B merely contains water molecules, hydrogen ions and electrons. The equation is always written in the direction of reduction, then it is reduced to 0:



In case of given compounds the equation practically contains two independent variables, namely the potential which is connected with the electron transition and the pH, i.e. the hydrogen ion concentration. The above equation written in a similar form

$$\sum_{\gamma} \nu_{\gamma} M_{\gamma} + ne^{-} = 0$$

where  $M_{\gamma}$  represents components taking part in the reaction (activity, fugacity).

Using the chemical potential of these components:

$$-\sum_{\gamma} \nu_{\gamma} \mu_{\gamma} + 23,060 nE = 0,$$

where  $\mu_{\gamma}$  = chemical potential and  $E$  the electrode potential.

This equation fulfills the condition that an equilibrium state between two different states of the system may occur only if the maximum useful work of the reversible state equals to zero. Since in the present case metal passes from the electrode into the solution, the work is done not only owing to the different chemical potentials of the metal and the dissolved ions, but to the different electric potentials prevailing in the double layer formed at the phase border. Multiplying factor 23,960 is, however, necessary for the common nominator since chemical potentials usually are given in Kcal/mole. (1 eV = 23,060 Kcal/M).

$$\mu_{\gamma} = \mu_{\gamma}^{\circ} + RT \ln M$$

where  $\mu_{\gamma}^{\circ}$  is the chemical normal potential.

Substituting into the former equation

$$RT \sum_{\gamma} \nu_{\gamma} \ln M_{\gamma} = - \sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^{\circ} + 23,060 nE.$$

When the temperature is 25 °C ( $R = 1,987$  cal/degree)

$$592,5 \sum_{\gamma} \nu_{\gamma} \ln M_{\gamma} = - \sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^{\circ} + 23,060 nE.$$

On applying decimal logarithm:

$$1363 \sum_{\gamma} \nu_{\gamma} \log M_{\gamma} = - \sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^{\circ} + 23,060 nE$$

$$\sum_{\gamma} \nu_{\gamma} \log M_{\gamma} = \frac{- \sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^{\circ}}{1363} + \frac{nE}{0,0591}$$

$$\frac{0,0591}{n} \sum_{\gamma} \nu_{\gamma} \log M_{\gamma} = - \frac{\sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^{\circ}}{23,060 n} + E$$

Written in other form:

$$\sum_{\gamma} \nu_{\gamma} \log M_{\gamma} = \log K + \frac{nE}{0,0591}$$

and

$$E = E^{\circ} + \frac{0,0591}{n} \sum_{\gamma} \nu_{\gamma} \log M_{\gamma}$$

where  $K$  = equilibrium constant,  $E^{\circ}$  = electrochemical normal potential.

Therefore

$$\log K = -\frac{\sum \nu_{\gamma} \mu_{\gamma}^{\circ}}{1363} \quad \text{and} \quad E^{\circ} = \frac{\sum \nu_{\gamma} \mu_{\gamma}^{\circ}}{23,060 n}$$

In a fuller form

$$\log K = -\frac{a\mu_{\text{A}}^{\circ} + b\mu_{\text{B}}^{\circ} + c\mu_{\text{H}_2\text{O}}^{\circ} + m\mu_{\text{H}^{+}}^{\circ}}{1363}$$

and

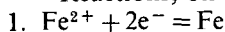
$$E^{\circ} = \frac{a\mu_{\text{A}}^{\circ} + b\mu_{\text{B}}^{\circ} + c\mu_{\text{H}_2\text{O}}^{\circ} + m\mu_{\text{H}^{+}}^{\circ}}{23,060 n}$$

From these formulas the equilibrium conditions of any chemical or electrochemical reaction can be calculated if the standard chemical potential of the components,  $\mu^{\circ}$ , or the value of  $K$  or  $E^{\circ}$  are known, determined from the chemical potentials. Below POURBAIX-diagrams of some sulfide ores investigated are demonstrated. Thermodynamic data required for the construction of the diagrams are taken from V. M. LATIMER's book [1950].

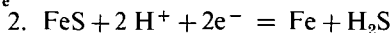
The Eh—pH diagrams of the metal-sulfur-water ternary systems were constructed relying upon the following reactions: dissolution of metals, formation of metal sulfides in the course of the reaction of the metal and hydrogen sulfide, dissolution of metal sulfides, their oxidation to metallic oxides and metal hydroxides, resp., when elementary sulfur was precipitated.

#### POURBAIX-diagram of the system Fe-S-H<sub>2</sub>O

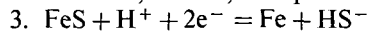
Reactions, on the basis of which the diagram was constructed, are:



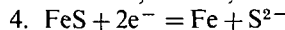
$$E = -0,441 + 0,0295 \log a_{\text{Fe}^{2+}}$$



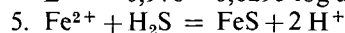
$$E = -0,334 - 0,0591 \text{ pH} - 0,0295 \log p_{\text{H}_2\text{S}}$$



$$E = -0,564 - 0,0295 \text{ pH} - 0,0295 \log a_{\text{HS}^{-}}$$

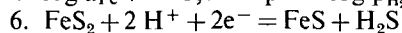


$$E = -0,970 - 0,0295 \log a_{\text{S}^{2-}}$$

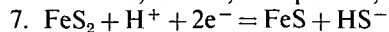


$$\log K = -3,7$$

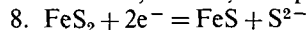
$$\log a_{\text{Fe}^{2+}} = 3,7 - 2 \text{ pH} - \log p_{\text{H}_2\text{S}}$$



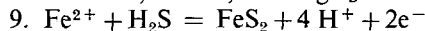
$$E = -0,187 - 0,0591 \text{ pH} - 0,0295 \log p_{\text{H}_2\text{S}}$$



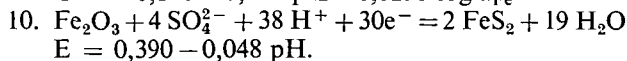
$$E = -0,423 - 0,0295 \text{ pH} - 0,0295 \log a_{\text{HS}^{-}}$$



$$E = -0,837 - 0,0295 \log a_{\text{S}^{2-}}$$



$$E = -0,140 - 0,118 \text{ pH} - 0,0295 \log a_{\text{Fe}^{2+}}$$



$$E = 0,390 - 0,048 \text{ pH}.$$

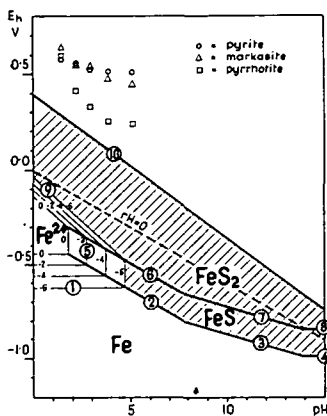


Fig. 1. Eh—pH diagram of the system Fe-S-H<sub>2</sub>O

Numbers on the diagram represent the reaction with corresponding order No, by which the given straights could be determined. Points marked with o are measurement data.

### POURBAIX-diagram of the system $\text{Zn-S-H}_2\text{O}$

1.  $\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$   
 $E = -0,763 + 0,0295 \log a_{\text{Zn}^{2+}}$
2.  $\text{ZnS} + 2\text{H}^+ + 2\text{e}^- = \text{Zn} + \text{H}_2\text{S}$   
 $E = -0,775 - 0,0591 \text{ pH} - 0,0295 \log p_{\text{H}_2\text{S}}$
3.  $\text{ZnS} + \text{H}^+ + 2\text{e}^- = \text{Zn} + \text{HS}^-$   
 $E = -1,00 - 0,0295 \text{ pH} - 0,0295 \log a_{\text{HS}^-}$
4.  $\text{ZnS} + 2\text{e}^- = \text{Zn} + \text{S}^{2-}$   
 $E = -1,415 - 0,0295 \log a_{\text{S}^{2-}}$
5.  $\text{Zn}^{2+} + \text{H}_2\text{S} = \text{ZnS} + 2\text{H}^+$   
 $\log K = 0,132$   
 $\log a_{\text{Zn}^{2+}} = -0,132 - 2 \text{ pH} - \log p_{\text{H}_2\text{S}}$
6.  $\text{Zn}^{2+} + \text{S} + 2\text{e}^- = \text{ZnS}$   
 $E = 0,174 + 0,0295 \log a_{\text{Zn}^{2+}}$
7.  $\text{Zn}(\text{OH})_2 + \text{S} + 2\text{H}^+ + 2\text{e}^- = \text{ZnS} + 2\text{H}_2\text{O}$   
 $E = 0,519 - 0,591 \text{ pH}$

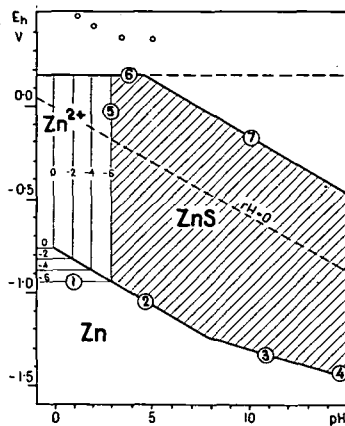


Fig. 2. Eh-pH diagram of the system  $\text{Zn-S-H}_2\text{O}$

### POURBAIX-diagram of the system $\text{Pb-S-H}_2\text{O}$

1.  $\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$   
 $E = -0,125 - 0,0295 \log a_{\text{Pb}^{2+}}$
2.  $\text{PbS} + 2\text{H}^+ + 2\text{e}^- = \text{Pb} + \text{H}_2\text{S}$   
 $E = -0,310 - 0,591 \text{ pH} - 0,0295 \log p_{\text{H}_2\text{S}}$
3.  $\text{PbS} + \text{H}^+ + 2\text{e}^- = \text{Pb} + \text{HS}^-$   
 $E = -0,545 - 0,0295 \text{ pH} - 0,0295 \log a_{\text{HS}^-}$
4.  $\text{PbS} + 2\text{e}^- = \text{Pb} + \text{S}^{2-}$   
 $E = -0,96 - 0,0295 \log a_{\text{S}^{2-}}$
5.  $\text{Pb}^{2+} + \text{H}_2\text{S} = \text{PbS} + 2\text{H}^+$   
 $\log K = 6,23$   
 $\log a_{\text{Pb}^{2+}} = -6,23 - 2 \text{ pH} - \log p_{\text{H}_2\text{S}}$
6.  $\text{Pb}^{2+} + \text{S} + 2\text{e}^- = \text{PbS}$   
 $E = 0,354 + 0,0295 \log a_{\text{Pb}^{2+}}$
7.  $\text{PbO} + \text{S} + 2\text{H}^+ + 2\text{e}^- = \text{PbS} + \text{H}_2\text{O}$   
 $E = 0,825 - 0,591 \text{ pH}$

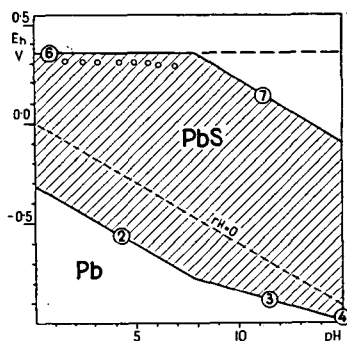


Fig. 3. Eh-pH diagram of the system  $\text{Pb-S-H}_2\text{O}$

### POURBAIX-diagram of the system $\text{Cu-S-H}_2\text{O}$

1.  $\text{Cu}_2\text{S} + 2\text{H}^+ + 2\text{e}^- = 2\text{Cu} + \text{H}_2\text{S}$   
 $E = -0,270 - 0,0591 \text{ pH} - 0,0295 \log p_{\text{H}_2\text{S}}$
2.  $\text{Cu}_2\text{S} + \text{H}^+ + 2\text{e}^- = 2\text{Cu} + \text{HS}^-$   
 $E = -0,499 - 0,0295 \text{ pH} - 0,0295 \log a_{\text{HS}^-}$
3.  $\text{Cu}_2\text{S} + 2\text{e}^- = 2\text{Cu} + \text{S}^{2-}$   
 $E = -0,900 - 0,0295 \log a_{\text{S}^{2-}}$
4.  $\text{CuS} + 2\text{H}^+ + 2\text{e}^- = \text{Cu} + \text{H}_2\text{S}$   
 $E = -0,084 - 0,0591 \text{ pH} - 0,0295 \log p_{\text{H}_2\text{S}}$
5.  $\text{CuS} + \text{H}^+ + 2\text{e}^- = \text{Cu} + \text{HS}^-$   
 $E = -0,340 - 0,0295 \text{ pH} - 0,0295 \log a_{\text{HS}^-}$
6.  $\text{CuS} + 2\text{e}^- = \text{Cu} + \text{S}^{2-}$   
 $E = -0,730 - 0,0295 \log a_{\text{S}^{2-}}$

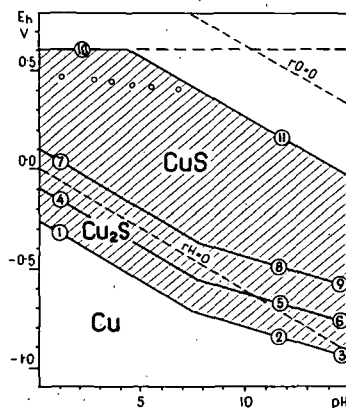


Fig. 4. Eh-pH diagram of the system  $\text{Cu-S-H}_2\text{O}$

7.  $\text{CuS} + 2\text{H}^+ + 2\text{e}^- = \text{Cu}_2\text{S} + \text{H}_2\text{S}$   
 $E = 0,100 - 0,0591 \text{ ph} - 0,0295 \log p_{\text{H}_2\text{S}}$
8.  $2\text{CuS} + \text{H}^+ + 2\text{e}^- = \text{Cu}_2\text{S} + \text{HS}^-$   
 $E = -0,126 - 0,0295 \text{ pH} - 0,0295 \log a_{\text{HS}^-}$
9.  $2\text{CuS} + 2\text{e}^- = \text{Cu}_2\text{S} + \text{S}^{2-}$   
 $E = -0,539 - 0,0295 \log a_{\text{S}^{2-}}$
10.  $\text{Cu}^{2+} + \text{S} + 2\text{e}^- = \text{CuS}$   
 $E = 0,600 + 0,0295 \log a_{\text{Cu}^{2+}}$
11.  $\text{Cu}(\text{OH})_2 + \text{S} + 2\text{e}^- + 2\text{H}^+ = \text{CuS} + 2\text{H}_2\text{O}$   
 $E = 0,862 - 0,0591 \text{ pH}$

These diagrams, constructed and calculated from thermodynamical data, are of theoretical character. It is an important problem to find suitable experimental methods to prove them. Methods for controlling the correctness of the calculated values have been elaborated by NAGEL, K. E. LANGE and R. OHSE [1957], then by J. HORVÁTH and L. HACKL [1965]. They have recognized the fact that when a voltage of constant intensity is applied from an outer source on a cell consisting of an electrode and a counter-electrode dipped into an electrolyte, and this current is stopped after some time, a potential value characteristic for the electrode to be investigated can be measured on the effect of the given impulse. The process which takes place can be interpreted in the following manner: the ohmic resistance caused by the electrolyte and the cover-layer on the metal exerts its effect in a few  $\mu\text{sec}$  after switching on the current, and there is a sudden change of the potential. After certain time an electric double layer is formed on the border surface of the metal and the electrolyte, resulting in a nearly constant electrode potential in consequence of the electrode processes taking place very rapidly. When the potential changes again, that is the concentration polarisation gets dominating, the current must be stopped. Then the reverse of the former process takes place. When on the effect of the outer voltage a new potential-determining process starts on the surface of the electrode, the potential measured after the stop of the current corresponds to the equilibrium potential of the electrode reaction. With corresponding technical devices J. HORVÁTH and L. HACKL [1965] succeeded in measuring for metals values agreeing with potentials calculated from thermodynamical data.

For a special study of the oxidation relations of rocks, methods have been developed by Soviet researchers, referred to by M. BOD and GY. BÁRDOSSY [1959]. Its essence is that extremely finely grained rock powder is saturated up to normal moisture content with distilled water via capillary absorption. Into the moistened rock powder platinum and calomel electrodes are placed, measuring the potential differences as well as the pH. The obtained equilibria values are regarded as the „redox potential” of the questioned rock. The above mentioned authors, considering that the pH of the rocks is about 6—8, at which value most of the elements with altering ionization state dissolve hardly or not at all, treated the samples with strong oxidizing agents so that processes leading to the change of the potential, occur. Sulfuric acid-potassium dichromate solution had been applied as oxidizing agent. Essentially this is an indirect method, since it is not the redox potential of the rock which is observed, but the change in the redox potential of the potassium dichromate system. In our opinion the values thus obtained do not agree with the redox potential of the rock, being a value of theoretical character, practically unattainable.

The above mentioned measurement methods applied after the required modifications, may largely contribute to a more detailed knowledge of processes occurring in the weathering of sulfide ore deposits.

In the course of the present study we were looking for an answer of the potential values of electrodes prepared from the sulfides to be investigated against saturated calomel electrodes, on the one hand in solutions with concentrations corresponding to natural mine water in neighbourhood of sulfide ore deposits, containing own and foreign ions, respectively, and in solutions having different pH. The question may also arise whether the potential values thus obtained can be reproduced and are characteristic of the given sulfide mineral, and whether they can be correlated with the redox potential values of given systems, with data obtained through calculations.

## EXPERIMENTAL PART

For the experiments carefully selected ore samples, free of contaminations and inclusions, have been chosen, embedded into polymethyl-metacrylate, one side ground and polished. In order to secure an electric contact, a hole was drilled down to the ore through the acrylate sample-holder, a glass tube inserted and fastened with piceine into the hole. The tube was filled with distilled mercury which kept a wire the other end of which was connected with the measuring apparatus. The polishing of the surface was repeated prior to each experiment, in order to secure largely the same experimental conditions. The ore-electrode thus prepared was put into closed cell together with the connection tube of the saturated calomel electrode as well as the inlet and the outlet gas tubes. Thus the investigated galvanic cell is:

(+) metal sulfide | metal salt solution | saturated KCl | saturated calomel (-).

The concentration of the applied solutions was  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$  and in some cases  $10^{-1}$ , the pH was adjusted by sulfuric acid or nitric acid and sodium hydroxide, resp. The potentials were measured with a (Radelkisz) titrimeter supplied by a stabilized electrical source. Before starting measurements, that is prior to inserting the sulfide electrode,  $N_2$  was bubbled through the solution in the cell for ten minutes in order to expel air.

### *Relationship of the potential and ionic concentration*

Potentials of electrodes inserted into solutions with ions same as the cations of the ores investigated (pH=2) measured *versus* saturated calomel electrodes are given in Table 1.

Table 1

	concentration (mole/l)			
	$10^{-4}$	$10^{-3}$	$10^{-2}$	$10^{-1}$
	potential (mV)			
pyrite	383	426	482	515
marcasite	392	443	498	533
pyrrhotite	293	312	370	428
covellite	229	232	235	245
sphalerite	195	215	218	232
galena	29	40	60	75

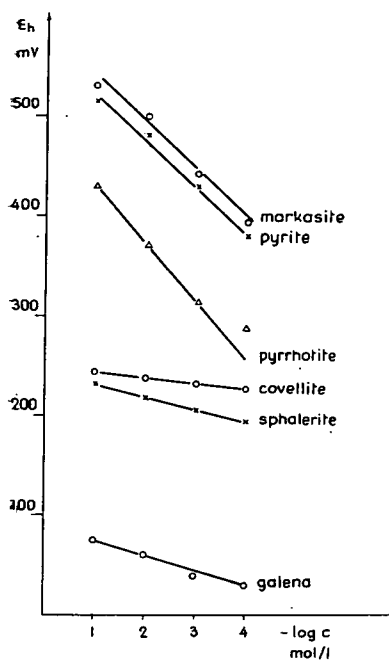


Fig. 5. Relationship of the potential and ionic concentration

the value of the electrode potential is also influenced by differences in the lattice structure.

#### Connection between the potential and the pH

This connection has also been studied in the case of the previous ores in solutions containing own ions with a concentration of  $10^{-2}$  mole/l *versus* saturated calomel electrodes. Measurement data are enlisted in Table 2.

Values measured for the study of the connection between the potential and the pH were recalculated for normal hydrogen scale and are drawn on the corresponding POURBAIX-diagrams obtained by calculations (marked with circles). In the case of natural sulfides it appears that by this method (which for ores from the same deposit renders a tolerably well reproducible determination of the potential values, thus it is possible to make conclusions on the weathering processes of a given mine) is impossible to measure potential values which would agree with those calculated from thermodynamical data and thus regarded as absolute ones. In some cases the same tendencies can be observed in the run of the straights connecting the measured and calculated points, but a numerical identity cannot be experienced. Literature contains several references concerning the fact that minerals primarily formed in great depth and at high temperatures getting into contact with the atmosphere undergo erosion, the latter being a process analogous to the corrosion of metals. Since we are in lack of corresponding methods this analogy experimentally has not been so far justified, although the intermittent galvanostatic polarisation method suggested by J. HORVÁTH and L. HACKL appears to be applicable even in case of sulfides, thus it serves as a basis for further investigations.

Data in Table 1 are means of repeated measurements. In one measurement the readings were done in the first, third and fifth minutes inserting the electrodes. Of these values only one, obtained in the fifth minute was considered in the mean value.

Inserting different sulfide ores into solutions of different concentration, containing own ions, the first thing to be stated is that they follow the NERNST-equation what means that the measured potential and the concentration of the solutions are in linear connection as shown in Fig. 5. Since in each case the anion of the solution is  $\text{SO}_4^{2-}$ , representing the more oxidized form in the system, the decrease of the concentration of  $\text{SO}_4^{2-}$  brings about the lowering of the potential in every case, of course in a rate depending on the system. It can also be stated that of the iron sulfides pyrrhotite shows the most rapid changes as it has the lowest potential. This is also indicated by the fact that in strongly acidic solutions (pH = 1–3) it is very difficult to obtain reproducible values for pyrrhotite since in acidic solutions it easily decomposes yielding  $\text{H}_2\text{S}$  and  $\text{Fe}^{2+}$  ions. In the case of pyrite and marcasite the values differ, what indicates that



Table 2

pyrite	pH mV	1,42 325	2,15 302	2,92 283	3,85 269	5,07 259			
marcasite	pH mV	1,42 378	2,15 298	2,92 284	3,85 222	5,07 200			
pyrrhotite	pH mV	1,42 340	2,15 155	2,92 70	3,85 2	5,07 —5			
covellite	pH mV	1,01 218	2,70 206	3,57 193	4,66 172	5,67 165	6,86 151		
sphalerite	pH mV	1,15 230	2,00 190	3,45 121	5,00 103				
galena	pH mV	1,67 65	2,50 62	3,11 61	4,15 58	4,98 58	5,62 49	6,10 43	6,91 40

*Connection between the potential and the foreign ion concentration in changing atmosphere*

For a better approach of natural conditions experiments have been done with solutions of different cations ( $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ) in the same concentration ( $10^{-2} - 10^{-6}$  mole/l) and in solutions containing all these cations as well (pH = 2). Measurement data are shown in Table 3. Measurements A, B and C are values obtained in air, without mixing, then on introducing nitrogen and air, respectively.

Of data in Table 3 values obtained in air without mixing (unbroken line) and those obtained when introducing air (broken line) were plotted in Fig. 6 as functions of concentration (pyrite x; marcasite o; pyrrhotite  $\Delta$  and sphalerite  $\square$ .)

Table 3

		concentration (mole/l)				
		10 <sup>-6</sup>	10 <sup>-5</sup>	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>
		potential (mV)				
pyrite	A	300	359	382	400	425
	B	375	385	387	392	412
	C	354	385	395	428	488
marcasite	A	365	382	395	425	482
	B	405	428	438	442	515
	C	405	415	430	464	493
pyrrhotite	A	240	462	300	345	381
	B	322	325	330	347	400
	C	310	328	337	354	390
sphalerite	A	110	140	170	208	275
	B	150	160	180	220	260
	C	174	198	223	273	309

As the run of curves shows, the measured potentials do not follow the NERNST-function when the solutions applied as electrolytes contain simultaneously more cations in the same concentration. Moreover, the measured potential values do not show a numerical agreement with those obtained for a sulfide electrode dipped into a solution with own ions, *versus* saturated calomel electrode. Since in natural mine water, being in contact with the ores, the simultaneous presence of several ions must be considered, the earlier observations have got experimental proof, namely that in the case of natural sulfides a generally valid potential series, similar to that of metals, cannot be compiled. This is further proved by the difference of the list according to increasing electrode potentials given by the results of the two former set of measurements, although here always a simplified form of the natural conditions is considered, since the solutions contain only  $\text{SO}_4^{2-}$  anions.

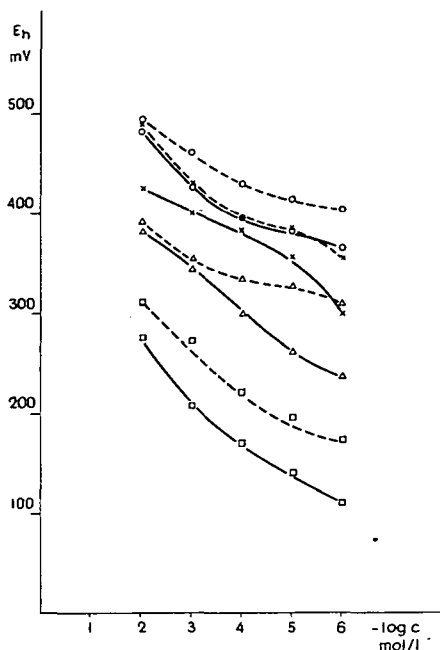


Fig. 6. Electrode potentials as functions of the concentration (in air without mixing: unbroken line; with introducing air: broken line)

of the air. Moreover, the process of weathering is accelerated by the difference of potentials owing to the atmospheric conditions existing between ores in the lower layers having no contact with air and those in the upper layers, when they get into ascribed to a wider contact with the oxygen contact through the downwards leaking mine water.

Potentials measured in the nitrogen stream numerically differ from the previous ones and they are not suitable for setting up a generally valid potential series.

#### Study of „mixed electrodes”

Experiments were also carried out to study what potential values can be measured *versus* saturated calomel electrode in the case of coupling several metal sulfide electrodes, namely of a „mixed electrode”.

As it is known the potential of the mixed electrode is the same as that of a one-component electrode made up of the less noble (i.e. having more negative potential) constituents in the same solution. The more noble part practically does not influence the potential supposed that the normal potentials of the metals are not too near each other — there is a difference of at least 50—100 mV.

First of all the potentials of the single electrodes have been measured — using sulfuric acid solutions of different concentration as electrolytes — *versus* saturated calomel electrode. These results are summarized in Table 4.

Table 4

	H <sub>2</sub> SO <sub>4</sub> concentration (N)			
	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-1</sup>
	potential (mV)			
pyrite ①	323	330	340	350
marcasite ②	348	357	365	375
pyrrhotite ③	275	277	290	320
sphalerite ④	110	120	135	155

As a second step the potential of the „mixed electrode” composed of two-two sulfides was also measured *versus* saturated calomel electrode, too, in sulfuric acid solutions with changing concentrations. Values thus obtained are given in Table 5.

Table 5

	H <sub>2</sub> SO <sub>4</sub> concentration (N)			
	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-1</sup>
	potential (mV)			
pyrite-marcasite ⑤	305	310	325	345
pyrrhotite-marcasite ⑥	306	310	333	376
pyrrhotite-sphalerite ⑦	195	206	242	320

In the measurement special care was taken that the connection tube of the calomel electrode was at the same distance from all the components of the „mixed electrode”. Connection between the measured potential values and sulfuric acid concentration are illustrated by Fig. 7.

Figure 7 indicates electrode potentials thus measured do not correspond to potentials of mixed electrodes taken according to the definition. In the case when two ores of different composition are coupled in the above described manner, in sulfuric acid solution with higher concentration a value equal to the potential of the two ores being the more noble, can be measured, i.e. which has a more positive electrode potential. Moving towards lower concentrations the measured potentials more and more approach the average value of the potential of the two coupled electrodes. This shows that changes taking place on the surface of both of the electrodes play a part in the determination of the potential.

If the pointed end of the connection tube of the reference electrode is placed near to any of the metal sul-

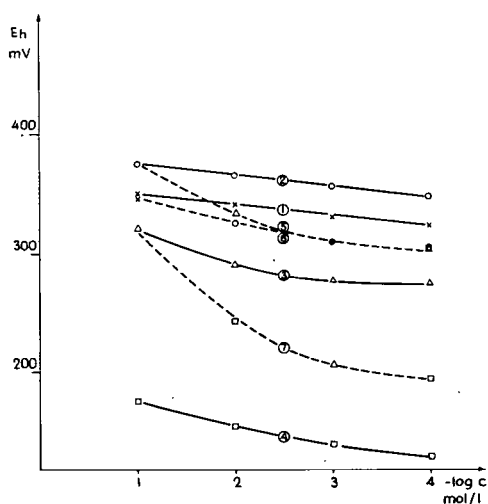


Fig. 7. Relationship of the potential of „mixed electrodes” and sulfuric acid concentration

fides, different potential values are obtained, which do not agree with, but are quite near those of the single electrodes.

Experiments to compose a „mixed electrode” have also been carried out in a way that plates cut off the different sulfides were bedded together. The embedding happened in Wood-metal, the contacting borders of the plates as well as the whole of the Wood-metal were covered with wax. „Mixed electrodes” thus prepared behaved similar as described previously.

These measurements likely prove the fact that to carry out processes taking place in nature, to control theoretical values in an experimental way is by far a complex problem even the conditions having been simplified to a very marked extent.

## SUMMARY

1. The connection between the potential and ion concentration in a solution with own cations likely follows the NERNST-equation, while it is not valid for solutions containing simultaneously several cations.

2. The study of the connection between the potential and the hydrogen ion concentration can be done only by special methods so that data, in agreement with the potential values calculated from thermodynamical data, be obtained.

3. Values received when applying different atmospheres yield information concerning the role of airing, influencing weathering.

4. It is not probable that formation of mixed electrodes play a part in weathering, merely galvanic elements could be formed, on the effect of which ores with more negative potentials suffer a more marked dissolution.

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MRS MARGIT AGÓCS  
Institute of Mineralogy, Geochemistry  
and Petrography  
Attila József University at Szeged  
Táncsics M. u. 2.  
Szeged, Hungary