

THE CHANGE OF THE ELECTRODE POTENTIAL OF SPHALERITE-PYRRHOTITE SYSTEMS AND ITS ROLE AT THE WEATHERING OF SULPHIDE ORE DEPOSITS

(Preliminary Report)

by MICHAEL NOVÁK and MARIA BÁN
Institute for Mineralogy and Petrography,
University of Szeged, Hungary

INTRODUCTION

The outcrop of sulphide ore deposits and their part beneath the surface, respectively, is exposed to the effect of chemical and physical factors of the weathering. The study of the oxidation processes taking place in the oxidation zone is essential also from the point of view that the cementation zone, often representing economically important and valuable mineral enrichment, forms in the deeper part of the ore body due to the action of metalbearing aqueous solutions seeping down from the oxidation zone.

The processes taking place at the weathering of sulphidic ore deposits earlier were interpreted as simple chemical reactions, the electrochemical properties of the single ores, however, were only less taken into consideration. The relatively few referring data of the earlier literature are comprised by *H. Schneiderhöhn* [1924] in his comprehensive work dealing with the mineralogy of oxidation and cementation zone, respectively.

The examinations mentioned above have dealt partly with the solubility relations of the single ores and the interaction referred to the solubility due to the contact of the ores, partly with the problem of the electromotive force series of the sulphide ores.

It is plausible that the solubility relations of the single ores are essential at the weathering of the ores and the formation of the oxidation and cementation zone. In the change of the solubility properties, however, the differences among the electrode potentials of the single ore minerals play an important role.

THE ELECTROMOTIVE FORCE SERIES OF SULPHIDE ORE MINERALS FROM
THE POINT OF VIEW OF THE INTERPRETATION OF THE WEATHERING

Recently, examinations regarding to the electromotive force series of these ores are carried out by *Rechenberg* [1951]. He used as electrolyte, not distilled water as *Gottschalk* and *Buehler* [1910], but solutions of different concentration and pH. On the basis of his examinations he stated that apart from minimal deviations the sulphide ore minerals in a given e. m. f. series can be arranged and the sequence of the minerals in this series is determined by structural properties. *Rechenberg's* opinion: the sequence according to the potential, recalculated to the normal hydrogen electrode, is analogous with the normal potential series of the metals.

The question is, whether it would be possible to establish a defined potential series of general validity referring to the sulphide ore minerals or not, and further, how far would such a series be applicable to interpret the weathering relations of single sulphidic ore deposits.

It is pointed to by *Grasselly* [1953] that while the potential series of the metals means the series according to the normal potentials, measured at exactly defined conditions, the normal potential of natural sulphide ore minerals can not be so simply established. The sulphide ores approach only exceptionally the ideal composition containing nearly always mechanical and/or isomorphous impurities in varying quantities, further, they are mostly in contact not alone with self-ionic aqueous solutions and the ion-concentration is also changeable. It seems to be more reliable studying the weathering of sulphide ore deposits that not so much the establishing of a defined potential series of general validity for sulphide ore minerals is essential, as the establishing of the potential series valid for the given deposit under the given circumstances, putting up this series by taking into account of the actual circumstances of the given deposit such as its mineral association, the actual composition of the ore minerals, their mechanical inclusions and isomorphous impurities, the pH and the composition and concentration of the aqueous solutions being in contact with the ores.

According to the above-mentioned, the potential of the single ore minerals gives some explanation regarding their solubility relations only in the case if these potential values are not taken into consideration in general, but are referred to the environment wherein the ores occur, because also the same ore mineral in an other occurrence can show partly an other potential value, partly also at the same potential value a different behaviour can be observed owing to the different environmental conditions.

Recently, *Noddack*, *Wrabetz* and *Herbst* [1955a, 1955b, 1956] have treated the electrode potential of natural and artificial sulphides not so much from geochemical but mostly from physico-chemical viewpoint.

According to their examinations most of the natural and artificial sulphides follow the *Nernst's* equation and in a galvanic cell, building with their own metal, they represent the positive pole. On the basis of the measured potentials, a defined electromotive force series is given

also by these authors. It is to be noted that in the series both natural and artificial sulphides are present. The authors pointed to that the results are strongly influenced by stoichiometrical deviations and by the presence of oxygen either on the surface of the electrodes or in the electrolyte.

The effects influencing the electrode potentials of the sulphide ore minerals are derived partly from the properties of the ore minerals themselves, partly from the properties of the environment. Thus, from the point of view of the electrochemical processes playing an essential role at the weathering, among others, also the changes in the composition of the ores, being caused either by mechanical inclusions or by isomorphous components, are to be taken into account.

THE EFFECT OF THE CHANGE OF THE Zn/Fe RATIO ON THE CHANGE OF THE ELECTRODE POTENTIAL OF SPHALERITES

The sphalerite-pyrrhotite system seemed to be very suitable to study the potential-influencing role of the isomorphous components, since partly the iron-containing sphalerite is common ore mineral of hydrothermal sulphide deposits, partly as in the sphalerite the zinc can be substituted by iron in considerable amounts and this solid solution in given cases may remain stable also by normal temperature. The iron content of the sphalerites depends upon the pressure and temperature at the time of its formation. The higher the formation temperature the greater amount of the zinc can be substituted by iron in the lattice of the sphalerite.

The question is whether the pyrrhotite content and its change in the sphalerites causes changes in the electrode potential of sphalerite and if it does, in what direction this change takes place. The purpose of the examinations was to establish the connection between the change of the pyrrhotite content and the electrode potential of the sphalerites, the direction of the probable change of the electrode potential and further to establish whether this change is unequivocal or not with the change of the iron content.

The measurements were carried out by Orion pH electrometer. The electrodes were sphalerite specimens from various localities. The Zn and Fe content of the samples were determined. Electrolyte was $ZnSO_4$ solution in various concentration. Reference electrode: n calomel electrode. The potential values in the Tables are those measured vs. n calomel electrode. At the grinding and polishing of the surface of the ore sections care was taken to have possibly identical surface quality in the case of each sample. The polished ore sections were also microscopically examined to find the part on the surface where it contains no or relatively few inclusions and thus to find the part designed to take up the cell containing the electrolyte.

The locality, the zinc and iron content and their ratio, respectively, as well as the measured potentials (vs. N. C. E.) of the samples are comprised in Table 1.

Table 1.

Locality	Zn %	Fe %	Zn/Fe	Potential in mV 0,01 m ZnSO ₄ pH 2,5
Rodna (Óradna, Rumania)	48	14,4	3,3	— 138
Herja (Kisbánya, Rumania)	42,8	12	3,5	— 78
Rodna (Óradna, Rumania)	54	11,9	4,5	— 105
Gyergyóholló (Rumania)	60,3	4,2	14,4	— 60
Gyöngyösoroszi (Hungary)	63	2	31	+ 230
Dognacea (Dognácska, Rumania)	52,4	1,7	31	+ 485
Baňská Stiavnica (Selmečbánya, Czechoslovakia)	63	1,8	35	+ 380
Picos del Europa (Spain)	66	0,33	200	+ 620

The data — despite of the relatively few samples — offer the possibility to answer the question. It can be stated that in the potential values of the sphalerites significant differences prevail presumably depending upon the iron content. The potential is more positive at low iron content whereas at higher iron content the potential is less positive or even negative *vs.* the normal calomel electrode. The potential becomes more positive with increasing Zn/Fe ratio.

However, at the same time can not be exactly stated that the change of the potential would be determined only and in every case, predominantly by the change of the iron content. There were samples, the potential of which, despite of the similar iron and zinc content and Zn/Fe ratios, respectively, were different. Slight or more considerable individual differences in potentials of the samples with similar iron and zinc content, however, do not change the tendency that the sphalerites with higher iron content, referring to higher formation temperature, possess in general rather negative potential whereas the sphalerites formed at lower temperature containing less iron, show an increasing positive potential with the decreasing iron content *versus* the normal calomel electrode.

The change of the potential of the sphalerite samples is in connection besides the iron content with other factors too, as e. g. the differences in granular structure of the specimens, the quality and quantity of the foreign inclusions at the surface of the polished ore section. The potential of the various sphalerite samples, is co-controlled by these factors too. It is also to be taken into consideration that the iron content of the sphalerites can be present not only as FeS in solid solution, but also as unmixed pyrrhotite lamellae or drops in the sphalerite. In the latter case the presence of several micro local elements at the surface of the polished ore section is to be taken into account and also these exert an influence on the average potential of the sample. That is, two sphalerite samples with the same iron content can possess different potential depending upon whether the iron, as solid solution or unmixed pyrrhotite inclusions, is present.

The electrode potential of sphalerites of different iron content changes between -138 mV and $+620$ mV *versus* the normal calomel electrode.

THE POSITION OF SPHALERITES FROM DIFFERENT LOCALITIES IN THE POTENTIAL SERIES OF SULPHIDE ORE MINERALS

It was already mentioned that several authors have determined a defined potential series for the sulphide ore minerals. From some point of view, however, may be questionable the suitability of putting up of such a potential series of natural sulphide ore minerals, considering this series as generally valid, and further, the rightness of the interpretation of the weathering of different sulphide deposits on this basis.

What does the position of single ore minerals in the potential series mean practically from the point of view of the weathering? It means that in the case of a polyminerale ore vein, the ore minerals of higher potential, in contact with ore minerals of lower potential, are rather protected from dissolution, whereas the ore minerals of lower potential behave anodic, i. e., they will dissolve and their solubility is greater than that of which could be established in the case of pure ore minerals in no contact with others.

Arranging the sphalerites from different localities on the basis of their electrode potential into the potential series proposed either by *Rechenberg* [1951] or *Wrabetz, Noddack and Herbst* [1955b], it can be stated that sphalerite samples can be ranged into both series in different positions, and the electrode potential and thereof the position in the series, further the behaviour of the different sphalerite specimens in contact with the other members of these series, roughly, is determined — with the reservations mentioned above — by the iron (pyrrhotite) content depending upon the locality, the conditions of the formation.

In our opinion the comparison with the potential series according to *Noddack, Wrabetz and Herbst* [1955b] seems to be rather reliable, though in this series besides the natural sulphides also artificial sulphides are involved, but the potentials are in self-ionic solutions measured, whereas the potential series according to *Rechenberg* [1951] contains alone natural sulphides, but the potentials are measured in solutions of foreign ions.

The fact that the various sphalerite specimens examined, in different positions can be ranged into the potential series considered of general character by the authors mentioned, may mean the following.

Table 2.

The position of sphalerite specimens from different localities
in the potential series of sulphide ore minerals
according to *Rechenberg* and *Noddack*, *Wrabetz* and *Herbst*

Potential series according to Noddack, Wrabetz and Herbst	Sphalerites, locality potential, iron content	Potential series according to Rechenberg
	Picos del Europa 620 mV; 0,33 %	
Ag ₂ S (art.) 579 mV	Dognacea 485 mV; 1,7 % Baňská Štiavnica 380 mV; 1,8 %	Pyrite 377 mV Marcasite 351 mV
CuS (art.) 319 mV		Chalcopyrite 277 mV
	Gyöngyösoroszi 230 mV; 2 %	
ZnS (nat.) 219 mV Cu ₂ S (art.) 199 mV		Sphalerite 178 mV
FeS ₂ (nat.) 139 mV		Pyrrhotite 117 mV Galena 114 mV
PbS (nat.) 89 mV		Argentite -5 mV
	Gyergyóholló -60 mV; 4,22 % Herja -78 mV; 12 %	
MnS (art.) -121 mV	Rodna -138 mV; 14,4 %	

The potential values are referred to normal calomel electrode.

While in the case of ideal or approximately ideal pure sulphide electrodes, among others in the case of ZnS electrode, a well defined potential value, and on the basis of such potential values, a defined potential series can be established, in the case of natural sulphide ore minerals as here, that is, in that of natural sphalerites of different localities and of different iron content, can not be generally spoken about *the* electrode potential of *the* sphalerite, because this potential value due to the action of several factors may be changed within wide limits. This consideration can not be limited only to the sphalerites, but it can be applied also to the natural sulphide ore minerals in general. In the nature the minerals, whose composition is close to the ideal ones are rather rare and the contamination of the ores by different foreign components is common. These mechanical and/or isomorphous impurities also in the case of the same mineral may be different depending upon the locality, the conditions of the formation and therefore, the same mineral occurring, however, in different localities,

having different electrochemical properties, from the point of view of weathering a diverse behaviour may show.

Thus considering the series of the sulphides, according to *Noddack*, *Wrabetz* and *Herbst* as well as *Rechenberg* in Table 2, if the potential series is considered as the potential series of the sulphides and the position of each mineral therein and the conclusions to be drawn are treated only in general, it can be stated that the sphalerite in both series is ranged approximately into the middle and the galena has a less positive potential than the sphalerite in both series, that is, in contact with galena the sphalerite will be protected from dissolution, whereas the solubility of galena becomes more considerable than if it were in no contact with sphalerite.

In spite of all, however, can not be supposed that in contact of the two minerals mentioned above, always the galena tends to dissolved and the sphalerite will be protected as the adverse case is possible too. Considering namely, the series of the sphalerites from different localities and assuming that the composition and thereof also the potential of galena varies between closer limits than that of the sphalerite, it can be assumed that even the sphalerite with higher iron content having thus a less positive potential than the galena, will dissolve in contact with the latter. So, it is presumable that sphalerites with higher iron content, e. g. sphalerites from Rodna or Herja, in contact with galena or pyrite, being of anodic character in this mineral-association, will rather dissolve. There again, the sphalerites with low iron content, e. g. sphalerites from Picos del Europa or Dognacea, in a mineral-association of sphalerite-pyrite-chalcopyrite-pyrrhotite-galena will be protected and rather the other members of this series will be dissolved.

Thus, on interpreting the weathering processes of given sulphide deposits on the basis of the electrochemical properties of the single sulphide ore minerals, not the electrochemical properties of the single sulphides in general, but always the actual conditions and circumstances of the given occurrence are to be taken into account.

The further examinations are in progress.

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