

SOME PROBLEMS IN DETERMINING THE OXIDATION STATE OF SEDIMENTARY ROCKS

Preliminary report

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INTRODUCTION

The determination of the oxidation state of sedimentary rocks may largely contribute to a detailed understanding of the conditions of sedimentation and of the nature of diagenetic processes, to the general characterization of sedimentary rocks as well as to the further development and refinement of their classification.

From the related literature many attempts are known concerning characterization of the "oxidation state" of sedimentary rocks and determination of "redox relations" or "reducing properties" of sediments.

The investigations aimed at the characterization of "oxidation state" of sedimentary rocks are connected both methodological and conceptional difficulties. A considerable part of methodological difficulties could be eliminated by introducing precise and accurate methods. As to the difficulties of principle we should like to refer to a remark of the classic work of ZOBELL [1946] according to which it is more easier to carry out precise measurements than to interpret the meaning of the results obtained.

Considering the foregoing investigations and the results and statements obtained, it seems that this complex of questions requires and — owing to its importance — also merits further studies.

Though the immediate aim of this preliminary report can only be sought in presenting some new aspects of the approach to the problems connected with the oxidation state of sedimentary rocks and in considering the possibilities of interpreting the measurements, it may be expected that the observations and reflections summarized below will contribute to a better understanding of this important and interesting problem.

SOME METHODS OF DETERMINING THE OXIDATION STATE OF SEDIMENTARY ROCKS

To determine the oxidation state of sedimentary rocks on the basis of chemical analysis, SZÁDECZKY-KARDOSS [1955] used the iron-oxidation-value
$$\left(O_{Fe} = \frac{2Fe_2O_3}{FeO} \% \right)$$
 and, he designed the place of different sedimentary rock

types in his system by using this value and the compound potential. The latter value can be calculated from the ionic potentials of the cations and anions present, taking into account the analytical data of the rock in question.

SZÁDECZKY-KARDOSS's system was successfully applied also by G. CSAJÁGHY [1965] for the geochemical classification of peloids rich in organic matter.

In characterizing the oxidation state of rocks by the iron-oxidation-value or oxidation grade, the meaning of this value is unequivocal. Some troubles may, however, arise in the case of peloids rich in organic matter because greater amounts of organic material, depending on its character, may interfere with the precise determination of the iron (II) concentration, diminishing in this way the reliability of the oxidation grade. The calculation of the average compound potential of the rock investigated may lead to further troubles, since this calculation would involve the total chemical analysis of the rock, though in his work referred to, SZÁDECZKY-KARDOSS gives the average compound potentials for different types of sedimentary rocks.

The oxidation grade used in the above conception for characterizing the oxidation state of rocks turns our attention towards the group of considerations which try to characterize the oxidation state by the oxidation-reduction relationship.

KRUMBEIN and GARRELS [1952] classified the chemical sediments on the basis of the Eh and pH of their environment, taking into account the Eh and pH conditions under which the mineral phases of given sediments may be precipitated from their solutions and may be considered as stable, respectively. The classification of mineral facies by SHTCHERBINA [1939] was also based on redox potential values.

It is, however, a different problem to determine, on the one hand, the probable conditions of formation of the main sedimentary rock types and their field of stability in function of Eh and pH, and, on the other hand, to find a way of determining the oxidation state or reducing properties of the rocks themselves. The oxidation state of the rock undeniably reflects in a lesser or greater degree the effects of the oxidation-reduction relationship prevailing during the formation of the sediment as well as the postdepositional changes in Eh and pH of their environment. In our opinion, the very origin of the problems of principle lies in trying to determine and characterize the oxidation-reduction properties of given sedimentary rocks.

BOD and BÁRDOSSY [1959] in their detailed investigations developed a new method of determining the oxidation-reduction relationship of sedimentary rocks. Their method essentially consists in introducing the powdered rock sample in sulphuric acidic potassium dichromate solutions of different concentration (0.001 to 0.1 N) and measuring the changes in potential of the solutions as a function of time. The changes in potential measured at the time t_1 and t_{24} 1 hour and 24 hours after the beginning of the run, respectively allow to draw conclusions concerning the oxidation state of the sample, its resistivity against oxidation, as well as the character of oxidation-reduction processes taking place. The potential changes measured in potassium dichromate solutions of different concentration will be the lower the stronger oxidized the rock is, and therefore, the less its effect in changing the potential of the solution. In the case of more reduced rocks greater changes of the potentials will be observed. If the stability of the rock against oxidizing agents is lower, so that, the oxi-

dation proceeds quickly already in the beginning, potentials measured at the time t_1 and t_{24} , respectively, will show less differences. On the contrary, if the rock is resistive against oxidation, the potential of the solution will change only gradually and consequently greater differences between the potential values measured at the time t_1 and t_{24} , will be found.

A. A. DROZDOVSKAYA [1963] dealing with the method of BOD and BÁRDOSSY, stated that though the method can be easily carried out and gives the possibility to compare different rocks concerning their oxidation state, the interpretation of the data obtained, however, is rather complicated and involves much graphical work.

Essentially, the difficulties mentioned in the introduction are met again, namely it is possible to measure certain values accurately and reproducibly, but the question as to the exact meaning of the values obtained invariably subsists, the more as even the authors referred to emphasized that the potential measured with their method is not equivalent with the "redox potential" of the rock.

It seems obvious that the best approach to the interpretation of the measurements can be found by elucidating the role of the different factors present in the system in producing the potential measured, and by determining the character and the amount of their contribution to the measured potential value, the potential in an aqueous suspension of the powdered rock sample being obviously a resultant of the interaction of all contributing factors.

ZOBELL [1946] in his paper on the redox potential of marine sediments applies the *reducing capacity* for characterizing the reducing properties of the sediments.

By definition, the reducing capacity means the quantity of oxidizing agent necessary to change the potential of the system by 1 Volt, i. e. the reducing capacity may be expressed as

$$\frac{\Delta C}{\Delta E} \left(\frac{\text{Moles}}{\text{Volts}} \right).$$

In marine sediments redox systems with different redox potential within a wide range may be present and, according to their character, they will play different roles in influencing the reducing capacity of the system. Non-consolidated marine sediments, rich in organic matter, generally show higher reducing capacities. The development of the reducing conditions is partly connected with the presence of H_2S , however, in many of the sediments iron(II) may also act as an important reducing factor. Furthermore, the organic matter itself can also have reducing effects.

To determine the reducing capacity e. g. of soils, STURGIS [1936] used diluted solutions of potassium dichromate containing potassium sulphate, and he calculated the reducing capacity by determining iodometrically the decrease of the oxidizing agent in an aliquot taken after a certain time from the supernatant of the soil-suspension.

The method of TRASK and HAMMAR [1935] is similar in principle, except that they used chromic acid to determine the reducing capacity. BOD and BÁRDOSSY's method is based on the same principle, too.

The consumption of the oxidizing agent is determined by the interaction of several factors, so, of the quantity and oxidation state of the organic ma-

terial and the possibility of being oxidized under the experimental conditions; but, of course, the oxidizable inorganic compounds will also play a role.

According to ZOBELL, a source of error of the methods mentioned consists in the fact that on the one hand, some reduced organic components in the soil or in the sediment will not be oxidized and, on the other hand, less soluble reducing inorganic compounds will not be affected by the oxidizing agent. Furthermore, in sediments rich in organic matter the use of strong oxidizing agents is not favourable. In our opinion, the difficulties mentioned by ZOBELL unfortunately exist in every method known up to this day. The problem could be solved if it were possible to study the character and the extent of the effect of the different factors controlling the redox potential and reducing capacity of the system obtained from the suspension of the sediment separately.

An ideal oxidizing agent for determining the redox capacity of sediments containing organic matter should be one of relatively high Eh but not sufficiently oxidative to destroy the organic matter; it should only affect the reversible ox/red systems but not react with the components of the ox/red system.

ZOBELL proposed slightly acidic FeCl_3 solution as an oxidizing agent which, though not ideal, yet could be acceptably used for characterizing the reducing capacity of non-consolidated sediments rich in organic matter. He measured the potential in suspension, excluding the effect of atmospheric oxygen, then titrated the suspension with FeCl_3 solution, waiting for the equilibrium after the addition of each aliquot, then measured the Eh. He continued the Eh readings till the Eh did not change on addition of further drops of FeCl_3 solution. The reducing capacity of the sediment is characterized by the shape of the titration curve. He was able to show in this way that e. g. the reducing properties of three sediments, characterized by the trend of the curves, were different, though the starting Eh values of the suspensions were the same and the final Eh values at the end of the titrations were also equal.

EXPERIMENTAL

Experimental conditions

The aim of these preliminary investigations was to find an approach to the solution of two problems; namely

a) to attempt to reveal separately the factors controlling jointly in their interactions the course of the potential curve, provisionally outlining the possibilities at least and

b) to elaborate a way of expressing the reducing capacity of sedimentary rocks not only by the shape of the titration curves but possibly by a numerical value derived from the potential curve.

In performing the measurements, 0.05 M FeCl_3 solution was used as oxidizing agent, its pH being adjusted to ~ 3 to prevent hydrolysis. In a covered plastic cell 10 grams of rock ground to less than 0.06 mm grain size were suspended in 50 ml distilled water boiled and cooled to room temperature previously. The Pt-electrode, the gas-inlet-tube and the agar-agar — sat. KCl bridge connecting the cell with the saturated calomel reference electrode were introduced through the cover. The measurements were performed in nitrogen atmosphere, under continuous stirring with a vibrating stirrer.

After measuring the initial potential of the suspension, FeCl_3 solution was added by 0.5 ml portions. After each dosis, when a relative equilibrium had come about (3 to 7 minutes), the potential was read. The adding of the oxidizing agent was continued till a relatively constant potential was reached, then the potential (in mV) was plotted against the consumption of oxidizing agent (in ml).

In the *run 1* the potential curves of suspensions prepared from original, untreated rock samples were recorded. These curves are shown in *Fig. 1*. The samples were Lower Pannonian sedimentary rocks.

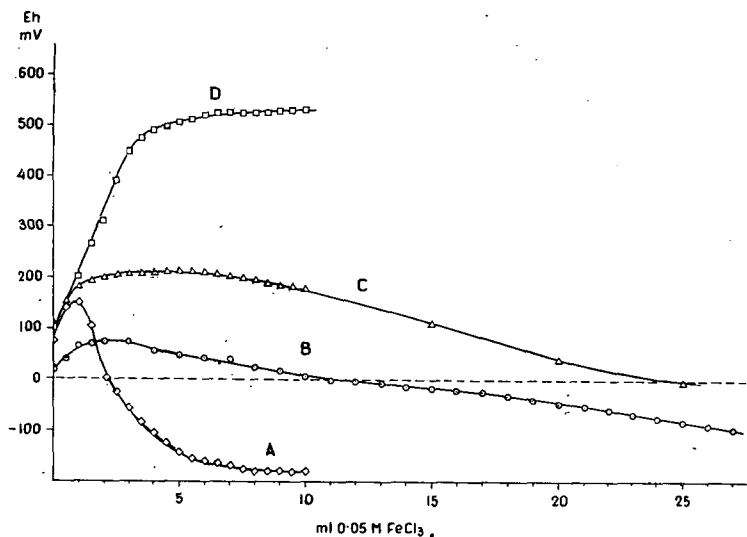


Fig. 1. Redox potential change of suspensions of different sedimentary rock samples in function of the quantity of the FeCl_3 solution added to the suspension.

Sample *A* is light gray, fine-grained-sandstone; in thin section very little carbonaceous plant remnants can be observed; the sample contains muscovite, biotite and chlorite.

Sample *B* is also a fine-grained sandstone with marly embeddings, with little carbonaceous plant remnants in some places and parts richer in muscovite and biotite.

Sample *C* can be described as a lime-marl without any characteristic features in thin section. After dissolution of the carbonates, the residue consisted of kaolinite, muscovite, chlorite, goethite and quartz, according to DTA and X-ray investigations.

Sample *D* is a sandy conglomerate; little abraded quartz pebbles and some feldspar was embedded in the coarse sandy fraction; in thin section besides relatively much muscovite, other phyllo-silicates could not be observed.

DTA curves of the mentioned samples are shown in *Fig. 2*. The differences in the carbonate content (magnesian limestone and calcite, respectively) of the

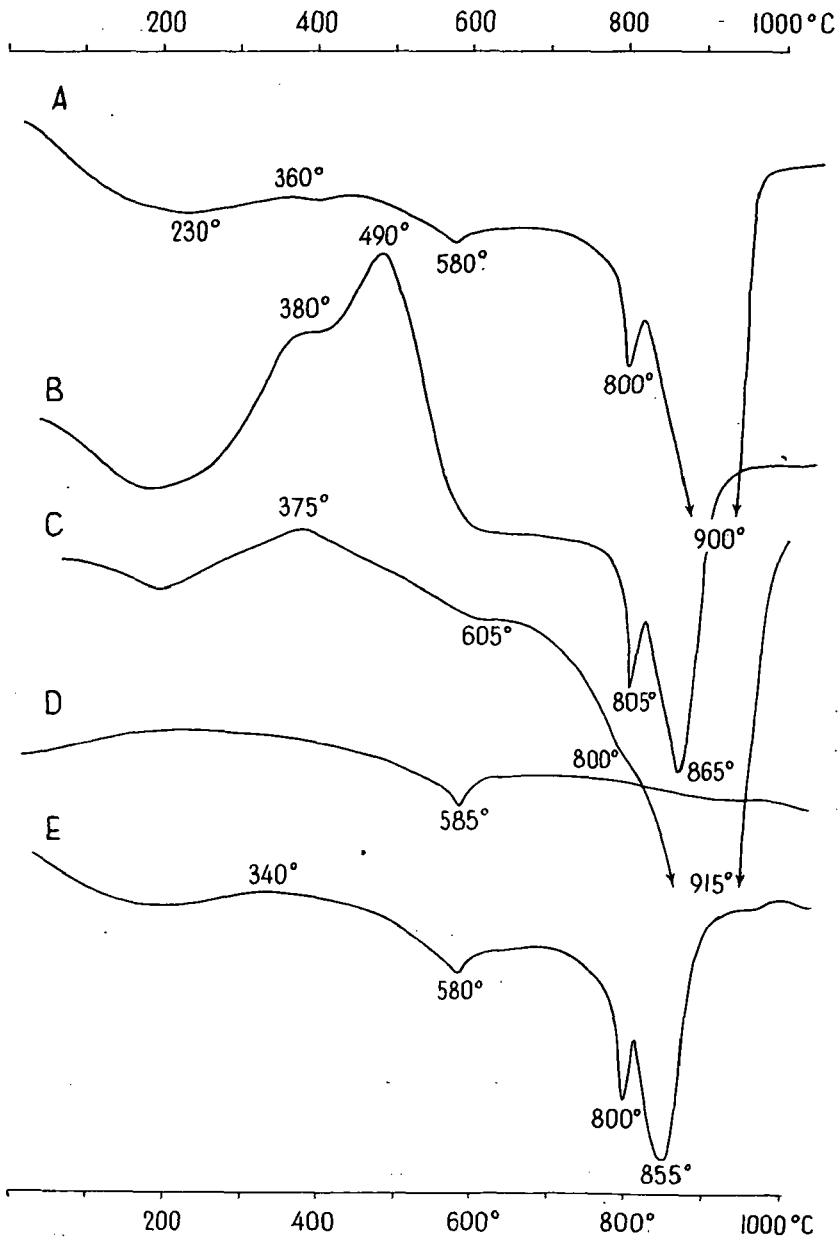


Fig. 2. DTA curves of the samples investigated (description of the samples see in the text).

samples can be well observed in these curves; the double exothermic peak between 415° and 490° C in curve *B* points to the organic matter content of this sample.

It seemed interesting to clear up whether the organic matter content of the samples exerts any influence on the potential curves and, if so, to determine the character of this influence. For this purpose sample *E* containing minimal quantities (0.16 per cent organic C) of organic matter was chosen. Sample *E* was also a fine-grained sandstone, with carbonate cementing material, embedded claystone pebbles, muscovite, subordinate quantities of biotite and sericitized orthoclase. The potential curve of sample *E* is represented by curve *E* in Fig. 3.

In the *run 2* three per cent of different kinds of natural organic matter were mixed to the powdered sample *E* and the titration curves of these suspensions, shown in Fig. 3, were recorded. The organic matters mixed to the rock *E* were the following:

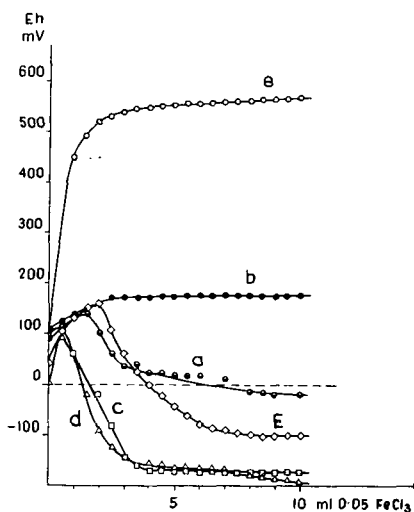


Fig. 3. Effect of different organic materials on the change of the redox potential curve of the same sample.

a) lignite (curve *a* in Fig. 3);

b) kerogen extracted from a rock sample rich in organic matter, according to the method described by FORSMAN and HUNT [1958]; it should be noted that this kerogene consisted not only of organic matter insoluble in organic solvents, but also contained little carbonaceous plant remnants and was contaminated by the admixture of some inorganic matter formed during the preparation (curve *b* in Fig. 3);

c) petroleum fraction distilled in the temperature range 280° to 300° C (curve *c* in Fig. 3);

d) petroleum fraction distilled in the temperature range 300° to 350° C (curve *d* in Fig. 3), and finally

e) petroleum fraction remaining in the flask after distillation up to 350° C (curve *e* in Fig. 3).

In the *run 3* the potential curves of twenty seven samples of sedimentary rocks, similar in character to those mentioned above, were recorded under the

same conditions. These curves are not shown separately; only the upper and the lower limiting curves of potential curves grouped according to their similar character, as well as the mean potential curves calculated for each group are presented in *Figs. 4, 5 and 6.*

Possible interpretation of the potential curves

Considering carefully the character of the curves in *Figs. 1 and 3*, three different types can be distinguished. In *type I* the potential of the suspension rises with increasing quantities of FeCl_3 , till, at a certain level, a relative equilibrium is reached. In the curves of *type II*, after an initial slight increase, the potential reaches a maximum, then it decreases again to attain a relative equilibrium at a low potential. The curves of *type III* range between type I and II; after a less pronounced initial maximum the potential decreases and approaches only very slowly an equilibrium.

In first approximation, the increase and decrease or the relative constancy of the potential can be brought into connection with the changes in concentration of the Fe^{3+} introduced in the system, i. e. with the concentration relationship of the ox/red system formed. A decrease of the Fe^{3+} concentration results in a decrease of potential, however, the decrease in Fe^{3+} concentration may occur not only in presence and as a result of reducing organic components but the adsorption of Fe^{3+} on the particles of the suspension, and/or hydrolysis can also lead to the same effect. Yet, should the decrease of the Fe^{3+} concentration and consequently that of the potential be effected by the latter process only, then the potential curve could hardly be considered as characteristic for the reducing property of the rock suspension.

Considering the potential curves shown in *Figs. 1 and 3*, it appears, however, that besides the possibility mentioned above, factors closely connected with the character of the rock play also a determinative role and so, the trend of the potential curve can be brought into connection with the peculiarities of the rock. Thus, the four rock samples of *Fig. 1* gave three different titration curves, and also the potential curve of the rock sample *E* in *Fig. 3* showed changes according to the character of the organic matter added to this sample.

As to the potential curves of *type I*, obtained e. g. with the rock sample *D* as well as with rock sample *E* containing kerogen or the residual petroleum fraction after distillation over 350°C , it seems that in case of curve *D* in *Fig. 1* and curve *e* of *Fig. 3*, on adding FeCl_3 the potential attains a relatively higher constant level corresponding to the concentration relationship of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system and further addition of FeCl_3 causes no further changes. It seems at the first sight, as if in the case of curve *D* in *Fig. 1* and curve *e* in *Fig. 3* components reducing the Fe^{3+} and thus diminishing the potential were not present or as if the Fe^{2+} concentration to be found in the sample were to low to cause a significant decrease in potential.

Curve *b* in *Fig. 3* is of similar character, however, the potential in its relatively constant interval is about 340 mV lower measured against saturated calomel-electrode. A possible interpretation of the difference between curves *b* and *e* in *Fig. 3* can be sought in the fact that in case of curve *e*, the 3% petroleum distillation residue added to the sample *E* and containing 87.04% C and 11.81% H proved to be free of sulphur, whereas in case of curve *b* the 3%

kerogen added to the same rock sample contained 6.22% S, and the presence of reducing sulphur compounds may diminish the Fe^{3+} concentration and thus the potential.

The relatively constant interval of curves *c* and *d* in Fig. 3 is even lower than the potential of the untreated suspension of the sample *E*. In the curves *c* and *d* the potential, after a slight initial rise, becomes constant at about -170 mV. The two curves of very similar character were measured in the suspension of the powdered rock which contained 3% of the petroleum fraction distilled from 280° to 300° C and from 300° to 350° C, respectively. The average composition of these two fractions is 84.80% C, 13.51% H and 1.58% N. As the original rock sample *E* was the same in each case and in

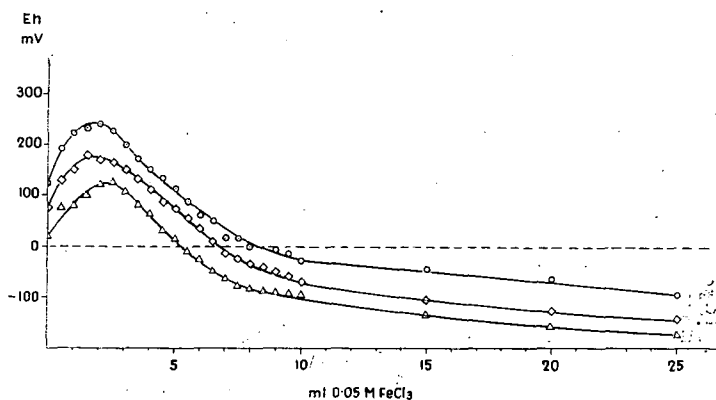


Fig. 4. Limiting and mean redox potential curves, respectively, characteristic of group I of the rock samples investigated.

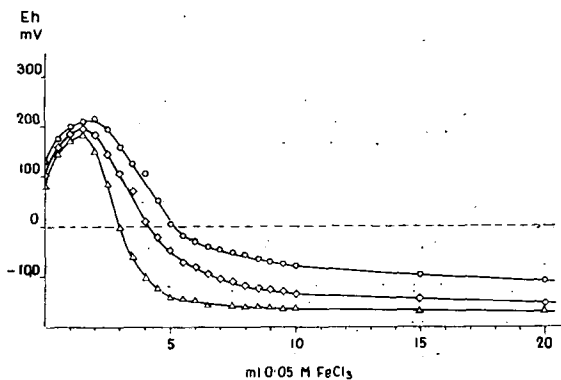


Fig. 5. Limiting and mean redox potential curves, respectively, characteristic of group II of the rock samples investigated.

presence of the components mentioned the potential was depressed with respect to that of the pure rock sample, it is obvious that the more pronounced decrease of the potential is to be ascribed to the reducing effect of the hydrocarbons added.

Carrying out the measurements with suspensions of numerous sedimentary rock samples mostly fine-grained sandstones with carbonate cementing material potential curves similar to curve *A* in Fig. 1 and curve *E* in Fig. 3 were obtained, as shown in Figs. 4 and 5.

In cases if the potential decrease cannot be attributed to reducing compounds or explained by the presence of reducing organic components, the question will arise, by what factor or what process the decrease in potential may be accounted for.

As briefly mentioned above, one of the possible answers may be found in making responsible the clay fraction or the fine-grained suspension itself for the decrease of the Fe^{3+} concentration, the Fe^{3+} being bound on the surface of the fine particles and/or the Fe(III) -hydroxide precipitated due to hydrolysis adsorbed on the surface of the fine particles.

This supposition seems to be supported by the fact that titration of the suspension of rock *E* with FeCl_3 solution of higher (0.25 M) concentration gave a curve which was initially similar to curve *E* of Fig. 3, but after the relatively constant section at a negative potential it began to rise again to approach a new equilibrium at a higher positive potential. This may be interpreted by assuming that the Fe^{3+} added to the suspension was gradually removed possibly due to adsorption, then after reaching the adsorption saturation, the further FeCl_3 added to the solution increased the Fe^{3+} concentration again and consequently the potential as well. It can also be assumed, however, that the Fe^{3+} concentration and the potential decreases due to the hydrolysis proceeding in the initial section, but later with the increase of the H^+ concentration in consequence of the hydrolysis, this process will cease and the addition of further FeCl_3 solution increases the Fe^{3+} concentration again, causing a further rise in the potential.

However, interpreting the trend of curve *E* in Fig. 3 on the basis of the above possibilities, the question arises why curves *b* and *e* in Fig. 3 are of different character, though they also represent potential curves of suspensions of the same rock *E*, with the difference that in case of curve *e* the suspension contained 3% of the residual petroleum fraction after distillation above 350°C and in case of curve *b* 3% kerogen. From a comparison of the curve *E* with the curves *b* and *e* in Fig. 3 it can be inferred that, taking into account the adsorption as a possible factor in the decrease of the Fe^{3+} concentration, the organic matter present, even without exerting an immediate reducing effect on the Fe^{3+} ions, in certain cases, depending on its character, may contribute to the constancy of the potential on a higher level, since in consequence of its more effective adsorption on the surface of the particles according to the supposition it will hinder the adsorption of Fe^{3+} ions and the decrease of their concentration and hereby also the decrease of the potential.

As a further and fairly conceivable possibility it can be suggested that the Fe^{2+} content in the samples may, at least as one of the several factors, contribute to the change of the potential by shifting the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in favour of latter and so diminishing the potential. It should be noted that the rock samples investigated mostly contained carbonates and presumably it is the Fe^{2+} content belonging to carbonates which may play such a role, whereas the Fe^{2+} of the silicates present will be less effective in diminishing the potential. For instance, the potential of the suspension of sample *D* in Fig. 1 became constant at a relatively high positive value; the carbonate content of the rock was insig-

nificant ($\text{CO}_2 = 0.22\%$) and the FeO content, which in absence of carbonates may be present in silicates, was 1.09% . On the contrary, the CO_2 content of sample *A* in Fig. 1 was 18.82% , its FeO content 2.45% and the corresponding values in sample *E* in Fig. 3 were 8.96% and 2.96% , respectively. The assumable trend of the FeO content of the samples to influence the potential curves can also be seen from the data of Table 1.

Determination of the reducing capacity of the sediments on the basis of potential curves

According to the purpose of this paper it has been tried to characterize the reducing capacity of the samples studied by numerical value derived from the potential curves. A relative equilibrium seems to be reached in the case of most samples, thus the reducing capacity can be expressed by the quotient of the oxidizing agent consumed up to the reaching the equilibrium (expressed in Moles) and the potential change (expressed in Volts).

The potential curves of the suspensions of the rocks studied could be classified as belonging to three types according to the faster or slower decrease in potential after the initial potential rise. In assigning the curves to the groups, the quantities of oxidizing agent used (in ml), corresponding to the point where the decreasing section of the potential curve intersects the 0 mV line, were taken into account. The limit between groups I and II was arbitrarily

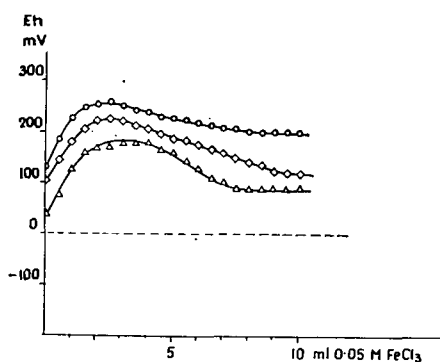


Fig. 6. Limiting and mean redox potential curves, respectively, characteristic of group III of the rock samples investigated.

chosen. The curves intersecting the 0 mV line below 5 ml consumption (Fig. 4) were assigned to *group I*, those intersecting this line above 5 ml consumption to *group II* (Fig. 5), whereas the potential curves which remained positive, at least under the conditions of the present investigations, were considered as belonging to *group III* (Fig. 6).

The mean values of the reducing capacity calculated from the curves grouped according to the above as well as the mean FeO contents of the groups are listed in Table 1.

Mean reducing capacity and FeO content of sedimentary rocks grouped according to their potential curves

Type	$\frac{\Delta C}{\Delta E} \cdot 10^3$	FeO %	Number of samples
I	3.3	1.91	7
II	6.5	2.67	9
III	13.9	3.82	11

From these investigations of informative character it can be inferred that the reducing capacity of the samples markedly depends on their FeO content; the latter is, however, to be considered only as one of several factors and its effect prevails mostly, or its role in the change of the potential becomes more evident, if the other components also affecting the potential are present in less significant quantities or are absent.

SUMMARY

To assess the reducing capacity of sedimentary rocks, the potential curves of suspensions of powdered rock samples were determined using 0.05 M FeCl₃ solution as oxidizing agent and plotting the measured potential values the quantity of oxidizing agent consumed. Similar measurements were carried out with the same rock sample with 3 per cent of different organic matter added. The organic substances used as additives were kerogen, lignite and different fractions of petroleum distillation, respectively.

The change in potential can be brought into connection with the concentration of Fe³⁺ added to the suspension; the potential is, however, influenced by several factors in a different grade.

The potential of the suspension may decrease owing to the adsorption of Fe³⁺ on the surface of the particles, but the concentration of Fe³⁺ may also decrease by hydrolysis. If these processes were the only factors causing the changes in Fe³⁺ concentration and thus the decrease of Eh, it would be difficult to find connections between the potential curve and the reducing property of the rock.

If the possibility of the adsorption exists, organic substances may hinder the adsorption of Fe³⁺ by being more strongly adsorbed on the surface of the particles and contributing hereby to maintain the potential on a higher level, provided that the reducing effect of some other factor does not intervene. This, possibility is perhaps displayed by curve *D* in Fig. 1 and curve *e* in Fig. 3.

Organic substances reducing the Fe³⁺ may also cause a decrease in potential, as shown e. g. in curves *c* and *d* in Fig. 3. Reducing sulphur-compounds or organic compounds forming complexes with Fe³⁺ may also lower the potential. Curves *b* and *a* in Fig. 3 may be considered as examples of this effect.

Besides the possibilities mentioned, the role of Fe²⁺ present in this samples in determining the trend of the potential curves seems to be emphasized by the above investigations. This role in decreasing the potential may be primarily attributed to the Fe²⁺ of the carbonates; the role of the carbonates themselves cannot be neglected either, especially if they are present in very small particle

size and in fine distribution, as in most of the samples investigated. The very fine grain size increases the solubility and this process may also contribute to the decrease in concentration of the Fe^{3+} added to the solution by promoting its hydrolysis.

The above possible processes will determine in their mutual interaction the potential curves recorded in the suspensions and the reducing capacity determined by the method used. The reducing capacity was determined from the titration curves and was expressed by the quotient of the quantity of the oxidizing agent used to reach a relative equilibrium and the respective potential change. According to these informative measurements the Fe^{2+} content of the samples seems to play a role in determining the reducing capacity.

We intend to study the possibilities mentioned above by model-experiments, in order to obtain a more detailed picture on the effect and the interaction of organic and inorganic factors determining the reducing capacity of sedimentary rocks.

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