INVESTIGATIONS ON OXIDATION-REDUCTION RELATIONS OF CONSOLIDATED SEDIMENTS BY ZOBELL'S METHOD

M. HETÉNYI and M. VÁRHELYI

INTRODUCTION

Elucidation of the oxidation state of sedimentary rocks may help in studying the processes of sedimentation in characterizing and in further refining the classification of sedimentary rocks.

The exact determination of the state of oxidation conceals several difficulties both in the practical measurement and in its interpretation.

KRUMBEIN and GARRELS [1952] classified the sedimentary rocks on the basis of theoretically calculated Eh-pH diagrams, designing the regions in which the given phase is stable or precipitates from the solution.

It is usual to characterize the state of oxidation of rocks by the ratio of the ferrous and ferric content, the so-called grade of oxidation. So BURRI used the formula $\dfrac{2[Fe_2O_3]}{2[Fe_2O_3]+[FeO]}$ for determining the grade of oxidation, while according to SZÁDECZKY-KARDOSS the *"iron-oxidation-value"* or oxidation grade (O_{Fe}) is given by the formula $\dfrac{2\,Fe_2O_3}{FeO}$.

The disadvantage of systems based on such considerations originates from the fact that the oxidation state of the rock as a whole is expressed by the oxidation-reduction relations of a single component.

Several authors tried to characterize the oxidation state by treating a suspension of the rock with oxidizing agents and measuring the change in potential of the suspension. As examples, the following may be mentioned:

STURGIS [1936] followed the progress of the oxidation process by measuring the change of the dichromate-content of samples taken in regular time intervals from the supernatant of the suspension.

BOD and BÁRDOSSY [1962] studied the changes in potential as a function of time in suspensions containing potassium dichromate acidified with sulphuric acid.

ZOBELL [1946] used the oxidation-reduction capacity for characterizing non-consolidated sediments rich in organic material. His aim was to find an oxidizing agent which does not destroy the organic material, neither reacts with the components of the rock, affecting only the reversible oxidation-reduction system. Giving ferric chloride solution in small portions to the aqueous suspension, the potential was measured after reaching the equilibrium. The addition of ferric chloride was continued until no change in potential could be observed. The reducing property of the sediments was characterized by the course of the potential curve.

It could be concluded from earlier investigations of one of the authors [GRAS-SELLY and HETÉNYI, 1970] that ZOBELL's method, with suitable modifications, could be used for characterizing the oxidation state of consolidated sediments, too. It was, however, necessary to find first a method for interpreting the potential curve and the factors determining its course.

Our aim was to characterize the oxidation state of different sedimentary rocks with potential curves obtained by potentiometric titration and by values calculated from the curves.
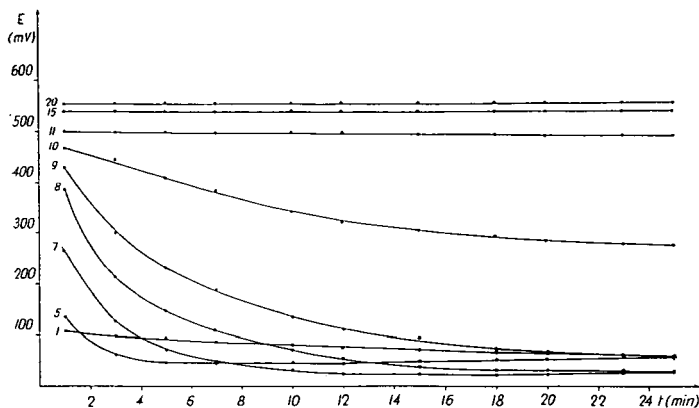

Fig. 1. The change of potential *vs.* time on addition of 1 to 20 ml 0.5 *M* FeCl₃

A necessary condition of the titration is a great change in free energy. If the difference between the normal potentials of the component participating in the reaction and of the titrating agent exceeds $4 \cdot 2.3 \cdot \dfrac{RT}{nF}$, then the change in potential is great enough in all kinds of electron transitions to permit the evaluation of the change in free energy. In the case of minor potential differences the titration curves can only be well evaluated by using a redox-system of greater difference in charge as oxidizing agent.

As the setting up of the equilibrium in the oxidation processes takes a certain time, for being able to determine the time necessary for attaining the equilibrium it proved necessary to measure the changes in redox potential as a function of time for the whole potential curve. Though most of the reversible oxidation-reduction processes are instantaneous ion-reactions, there may often occur secondary processes which also lead to equilibrium, but not instantaneously. Further, some time is necessary for the electrode to get into equilibrium with the solution and in different phases of the titration reactions of different velocity may occur.

Fig. 1 shows titration curves measured with different waiting periods. It can be seen from the curves that in different sections of the curves different time is necessary for reaching equilibrium. The equilibrium will be reached in 15—20 minutes in most cases. It is, however, necessary to remark that in model-experiments, especially if organic material is given to the system, or the samples contain originally organic material, much longer time is necessary to reach the equilibrium.

The measurement of the potential curve was carried out with the method described in the previous paper mentioned above. 5 g of the sample ground to 0,06 mm particle size were suspended in 100 ml dist. water and stirred with a magnetic stirrer. A Pt-electrode, a gas-inlet-tube for the nitrogen gas and an agar-agar bridge connecting the cell with a saturated calomel reference electrode were introduced through the cover.

The pH of the suspension was read at the beginning and after the end of the measurement. The oxidizing agent was added in portions of 0.5 ml, in certain potential ranges of 1.0 ml, the next portions being added after a relative equilibrium was reached.

The measured and calculated values used for characterizing the samples are the following:

Potential at saturation: E_{sat}

The quantity of oxidizing agent consumed up to the "point of inflexion": X

Slope of the curve: m

Reducing capacity: $\beta = \dfrac{\Delta c}{\Delta E}$

The reducing capacity indicates the change in redox-potential which can be reached by introducing a given external energy (oxidizing or reducing agent), i.e. the final state of energy of the system. Only few methods for characterizing the reducing capacity are found in literature.

MICHAELIS [1929] calculated by differentiating NERNST's equation for a system consisting of merely one redox-pair.

$$\beta = \frac{dx}{dE} = \frac{nF}{RT} x \frac{B-x}{B}$$

where B is the total concentration of the reduced and oxidized forms,
and x is the concentration of the oxidized form.

This formula is difficult to use in practice, because systems consisting of a single pair of redox partners are rarely found.

According to NIGHTINGALE the reducing capacity of the system is given by the quantity of the external oxidizing or reducing agent which changes the redox-potential of the system by one unit. This definition can be well used in practice in presence of several redox systems, independently of the knowledge of all occuring reactions.

The calculations carried out according to NIGHTINGALE's method were based on the experimental data of our potential curves. Thus difference quotients calculated for the total titration curves were used for characterizing the samples.

INTERPRETATION OF THE POTENTIAL CURVES

The course of the potential curve, i.e. the potential values measured, are determined by the rate of reduction of the $FeCl_3$ added to the suspension examined, and therefore by the concentration ratio Fe(II):Fe(III) found, which is decisive for determining the potential. As can be seen from *Fig. 2*, most of the potential curves begin with an almost linear section, in which the potential shows only slight fluctuations close to the initial value of Eh. As in the first section of the potential curve no significant changes in potential occur, despite the adding of $FeCl_3$ solution, processes decreasing the Fe(III) ion concentration may be supposed. All processes or factors decreasing the concentration of the Fe(III) added tend to decrease the po-
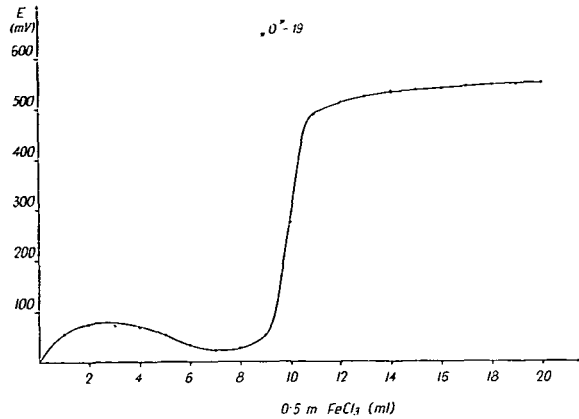
Fig. 2. Potential curve of sample "O—19"

tential. The decrease in Fe(III) concentration may also be due to the oxidation of some components of the suspension by the Fe(III) added. The change in the Fe(II): Fe(III) ratio may also be caused by Fe(II) ions dissolved from the rock, as well as by precipitation of the Fe(III) by hydrolysis, or by complex formation (e.g. in the presence of humic materials).
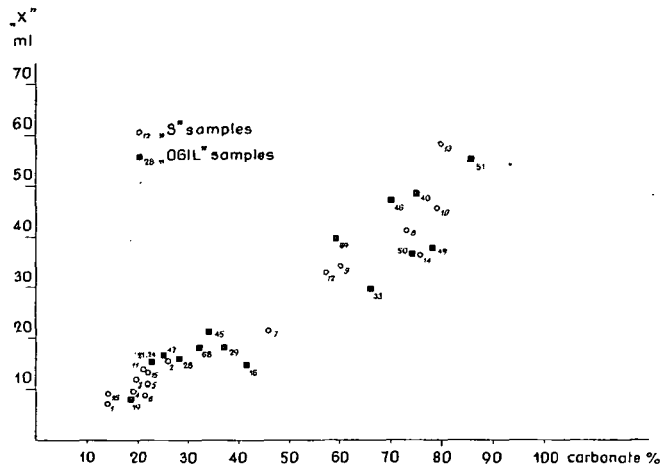

Fig. 3. Dependence of the value of X on the carbonate content of the samples

After these processes, as sudden increase in potential is observed in the solution, due to the increase in Fe(III) concentration. This is represented by section II of the potential curve.

In section III of the curve the potential becomes constant again corresponding to the Fe(II):Fe(III) ratio established.

It was attempted to find components and reactions playing a role in the different sections of the potential curve.

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Concerning section I, among the possibilities mentioned the influence of carbonates was studied in detail. The value of X (used for characterizing this section) changes linearly with the calcium-magnesium-carbonate content of the samples. To corroborate this relationship, model-experiments were performed. 1 to 5 %
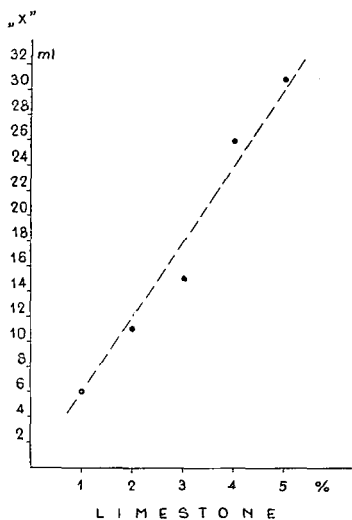

Fig. 4. Changes in X with increasing limestone content
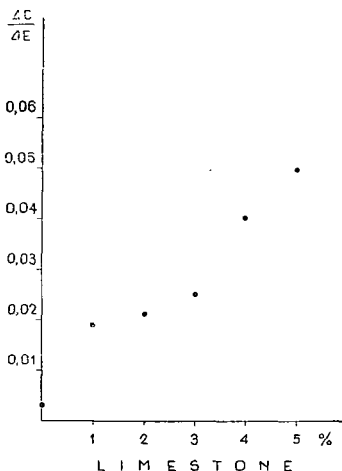

Fig. 5. Dependence of the redox capacity on the limestone content

limestone was added to a sample free of carbonate and the potential titration was carried out. Plotting the values of X as a function of the limestone content a linear relation was obtained (Fig. 4, 5). Hence, it may be concluded that section I of the potential curve i.e. the quantity of oxidizing agent consumed is determined by the carbonate content. Higher carbonate content may conceal the effect of less active components or those present in lower concentration; so the effect of the carbonate content will dominate in the characterization of the total curve, i.e. of the redox capacity, though it does not play any role in the redox process itself.

Section II of the curve, i.e. the rise in potential may be characterized by the slope of this section which is the steeper the higher the velocity of the reaction causing the rise. These parameters depend on the quality and oxidation state of the materials taking part in the reaction. To verify this supposition, the following experiments were performed: To a sample practically free of carbonate, 1 to 10 % of a petroleum distillation fraction (300—350 °C) was given, the titrations performed, and the slopes of the respective potential curves determined. Fig. 6 shows the slopes as
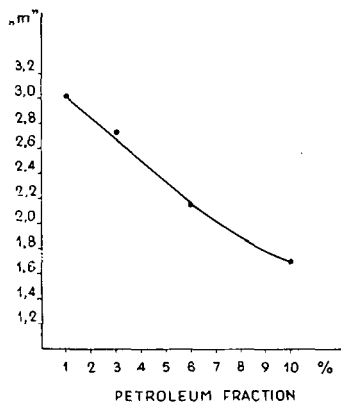

Fig. 6. Dependence of the slope of the potential curve on the quantity of petroleum distillation fraction added

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a function of the petroleum concentration. Then, adding lignite, car-bonaceous material and kerogen to the same sample, the potential curves were measured again and the slope of the curves was determined. Significant differences between the effect of kerogen and of carbonaceous material were observed *(Fig. 7)*; these may be due to the fact that the kerogen becomes more oxidized during the extraction. The influence of the carbonaceous material on the steepness of the potential curve is most important, its slope being greater by one order of magnitude compared with other materials.
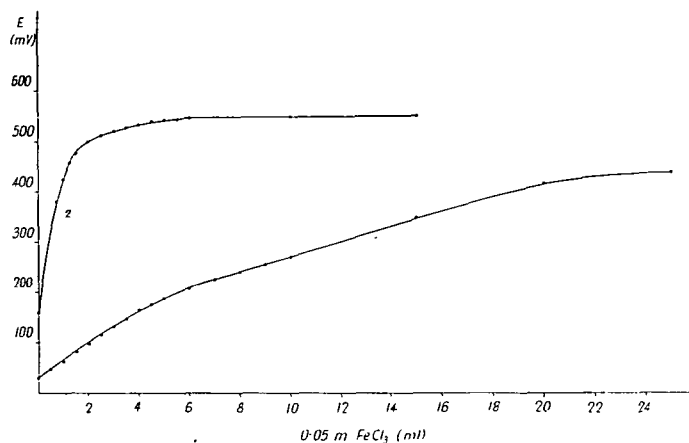

Fig. 7. Potential curves of coaly material *(1)* and of kerogen *(2)*

CALCULATIONS FOR CHARACTERIZING REDOX SYSTEMS

The fundamental electrochemical relationships cannot be applied in our calculations, since they hold only for reversible systems; hence, first of all, the reversible or irreversible character of the processes determining the potential is to be ascertained; further in most cases more than a single redox pair is to be taken into account. The reversibility is very important from experimental point of view because the redox capacity of irreversible systems is very low, and so, in measuring the redox potential instability may occur on the Pt-electrode.

According to EMSCHWILLER [1945] the reversibility or irreversibility of redox pairs is determined by the activation process of the system. The activation is composed of thermal and adsorptive activation. Thermal activation changes with concentration, while adsorptive activation is constant. If thermal activation is dominating in both the [ox] and [red] forms of a redox system, the system will be reversible, whereas it is irreversible if the activation is thermal in one form and adsorptive in the other. As activation=thermal activation+adsorptive activation, and one term of the expression being constant, in the extreme case of thermal activation=0, reversible systems will formally show irreversible behaviour. In reversible systems:

$$E_{ox}^0 > E_{redox}^0 > E_{red}^0 \cdot$$

In irreversible systems either E_{ox}^0 or E_{red}^0 can be reached and so

$$\text{either } E_{redox}^0 > E_{ox}^0$$
$$\text{or } \quad E_{redox}^0 < E_{red}^0 \cdot$$

Investigations on natural systems become more complicated by the fact that interactions between the different materials simultaneously present may occur. Simplification was attempted by basing the calculations on the most dominant system, while the others were neglected.

As the titration curve was used for characterizing the system and this curve was measured as a function of the quantity of the titrating agent, it was supposed that the potentials measured in the different sections were determined in the first line by the oxidizing agent used.

The suppositions concerning the quantitative decrease of the $FeCl_3$ added to the system were mentioned above; thus, among the possible equations given by POURBAIX for the Fe—H_2O system, the following were chosen for characterizing different sections of the titration curves.

In section I and II, supposing that hydrolysis is the factor determining the potential:

$$FeOH^{++} - Fe^{++} - H_2O + H^+ + e = 0 \tag{1}$$
$$E = 0.877 - 0.0591 \text{ pH}$$

$$Fe(OH)_3 - Fe(OH)_2 - H_2O + H^+ + e = 0 \tag{2}$$
$$E = 0.179 - 0.0591 \text{ pH}$$

For both sections, the calculated potential is the resultant of the values obtained from equation *1* and *2*.

In section III:

$$Fe^{+++} - Fe^{++} + e = 0 \tag{3}$$
$$E = 0.746 + 0.0591 \log \frac{[Fe^{+++}]}{[Fe^{++}]}$$

Adding 2, 3, 4 % limestone respectively or 2 % limestone and 3 % siderite to a rock originally free of carbonate, the potential curves were measured, interrupting the titration in each of the three sections, and the Fe(II) and Fe(III) content of the solution was determined where necessary for the calculation, the pH of the solution being measured during the whole run of the titration. The potential was calculated from the measurements. *Table 1* shows the difference of the potentials measured and calculated, expressed in mV.

In section III the difference between the measured and calculated values is not significant, especially taking into account the error of measurement of $+50$ mV given by ZOBELL; it should be remarked, however, that according to our experience, the error did not exceed about ± 10 mV. In this section it is really reaction 3 by

TABLE 1

Carbonate added to the rock	Difference between measured and calculated values of Eh in mV		
	Section I	Section II	Section III
2 % limestone	70	98	1
3 % limestone	37	5	7
4 % limestone	27	60	17
2 % limestone + +3 % siderite	16	81	5

which the potential is determined and the not too significant deviations observed are due to errors of measurement.

In sections I, II the occuring processes are too complicated to be exactly described on the basis of the measurements performed up to now. It seems probable that several processes ought to be taken into account. It is especially difficult to interpret the section II which represents a transitory state. The Fe(III) consuming process occured during section I; in section III the Fe(II); Fe(III) ratio characteristic for the given system has been already developed. While section I and III are more or less parallel to the abscissa, section II shows a steep rise. In this phase of the titration, important changes in potential are caused by addition of very small amounts of $FeCl_3$.

Taking into account also the above sources of error, the calculations presented in *Table 1* support the suppositions based on our measurements and verified by some model-experiments, namely that hydrolysis is the potential determining process in the first section of the titration.

Our measurements for studying some sedimentary rocks with the method described above led to the result that the differentiation between the types of the rock using $FeCl_3$ as oxidizing agent can be performed on the basis of the saturation potential. The starting potential of the suspension cannot be used for classification of samples, namely, it depends not so much on the oxidation state of the components, as rather on their solubility in water *(Fig. 8)*.

The saturation potential *(Table 2)* is suitable for differentiation of the groups, being 745 mV for manganese dioxide, 600 mV for bauxite, and 570 mV for quartzite;
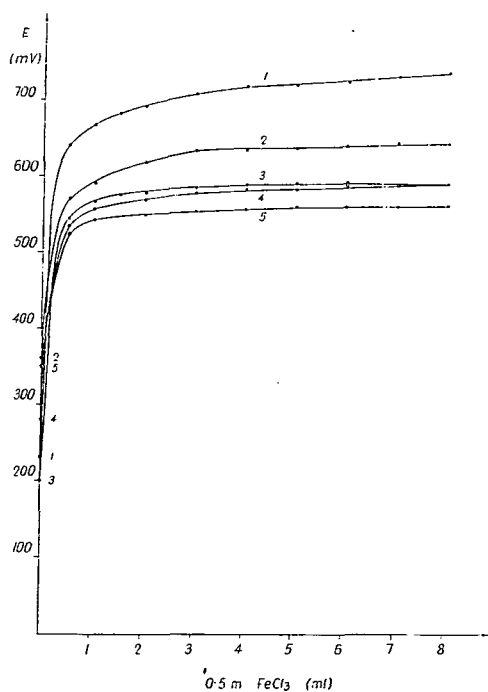

Fig. 8. Potential curves of sedimentary rocks of different type
1. Manganese oxide ore. *2.* Bauxite. *3.* Limey marl. *4.* Gypsum. *5.* Quartzite

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it cannot be used, however, for finer differentiation within the groups. We tried also to use other oxidizing agents, such as potassium permanganate, ceric sulphate. These proved less suitable for separating the different groups on the basis of the saturation potential, however, the saturation potentials of different samples within the same group generally presented greater differences than in the case of titration with $FeCl_3$.

TABLE 2

Type of the rock	Sample	E_{sat} 0.5 N $FeCl_3$	E_{sat} 0.01 N $Ce(SO_4)_2$	E_{sat} 0.01 N $KMnO_4$
Resistite	Permian Sandstone	625 mV	1150 mV	1060 mV
	Sandstone of Hárshegy	600	1140	1085
Siliceous rock	Chert	580	1125	1122
	Firestone	566	1150	1125
	Quartzite	568	1120	1110
Argillite	Fire clay	650	1160	1123
	Laterite	664	1175	1085
	Bauxite	660	1140	1095
Oxidite	Manganese oxide ore	745	1145	1040
Carbonate rock	Marl	595	1150	1090
	Limey marl	592	1150	1070
	Limestone	600	1170	1040
Reducite	Siderite	505	1190	998
Evaporite	Halite	667	970	1000
	Anhydrite	633	1150	1062
	Gypsum	602	1165	1135

It is to be expected that the oxidation state of sedimentary rocks determined by potentiometric titration may be useful in their classification. The results reached up to now are, however, only of preliminary character, designing the way to be followed.

It is to be supposed that further improvement of the method will permit to distinguish more sharply the different types of sedimentary rocks.

SUMMARY

Zobell characterized the oxidation-reduction state of non-consolidated sediments rich in organic material by potentiometric titration using diluted $FeCl_3$ solution as oxidizing agent. This method was applied for consolidated sediments, too.

The time necessary for establishing the relative equilibrium in oxidizing processes shows differences, depending on the type of the samples; 15—20 minutes, as a minimum, are necessary.

On the potential curve, generally three sections can be distinguished. Section I (the quantity of oxidizing agent consumed) is determined by the carbonate content of the samples, the hydrolysis being the potential determining process.

A steep rise of the potential is characteristic for section II, the slope of the curve depending ón quality and quantity of the organic material. By adding organic (kerogen and/or coaly) material to the system the potential rise can be decreased by an order of magnitude compared not only with different types of sedimentary rocks but also with samples containing petroleum distillation fraction as addition. The slope of the potential curves of samples containing kerogen was similar to that of rocks containing no (or very small quantities) of organic material. It can be supposed that the kerogen becomes more oxidized during the extraction.

Section III represents the equilibrium potential reached after the redox reaction.

The characterization of the systems by calculation is more difficult due to the complexity of the systems as well as to possible and uncontrolable secondary processes.

ACKNOWLEDGEMENT

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MISS DR. MAGDOLNA HETÉNYI,
MISS MAGDOLNA VÁRHELYI
Institute of Mineralogy, Geochemistry and
Petrography
Attila József University at Szeged
Táncsics M. u. 2.
Szeged, Hungary