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Model Studies on Redox Logging for Minerals

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Abstract. Physical models are prepared in the laboratory to study the variations of oxidation-reduction potentials in the simulated boreholes through the ore bodies and the surrounding media. The study reveals the following facts: (i) Redox logs will be useful for approximate delineation of depth and thickness of the mineralized bed (ii) Variations, rather than the absolute values of the redox potentials, will be of interest in redox logging (iii) Acidic borehole fluids are found to be better to sharpen the redox anomalies (iv) The redox potential is found to be almost independent of ore concentrations (from 10% to 80% by weight in plaster of paris model) with tap water (pH = 6.0) and other alkaline solutions as borehole fluid (pH = 7.0–12.0). Some trends of variations are observed for acidic borehole fluid (v) The changes in potentials per unit change in pH are found to differ widely for different minerals (vi) The redox potential value takes a significant time to remain stable over a time span of half an hour to one hour. The potential value changes significantly over a long time span. The values are not reproducible within 5% in most of the cases (vii) The potential changes considerably for every cleaning operation of the platinum electrodes.

Key words: Model experiment – Simulated borehole measurement of redox potential

1. Introduction

Oxidation-reduction potentials and the redox reactions are well known phenomena in electrochemistry. Even the existence of spontaneous flow of stationary currents (not telluric currents which are quasi-stationary) within the earth's sedimentary covers and the ohmic potential drop therefrom are known to the

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geophysicists for more than one hundred years. The surface measurements extend back to the work of Fox (1830). But the systematic use of the method started from about 1930. Since then an immense amount of field, theoretical and experimental works have been done to understand the variations of the self potentials (S.P.), which are primarily of oxidation reduction origin, near the ore bodies. Developments are done both on the theories of origin of S.P. and on the field data interpretation sides. Mention may be made of the following authors: Schlumberger et al. (1934), Poldini (1938), Heiland (1940), de Witte (1948), Yüngül (1950, 1954), Roy and Chawdhuray (1959), and Sato and Mooney (1960).

It has been realized since then that the electrochemical mechanism of self potentials, associated with the ore bodies, results from ohmic potential drops within the country rock. The current is produced by separable but simultaneous reduction of oxidizing agents near the surface and oxidation of reducing agents at depths. The ore body does not participate directly in either reactions but serves as a conductor to transfer electrons from the oxidizing agents to the reducing agents. Thus the surface self potential method of geophysical prospecting has become a fairly established method for the last 40 years and is used for shallow base metal sulphides, graphite, coal, etc. The convenience and ease in measurement and interpretation kept the method still alive. Here the geophysicists are primarily interested in the relative changes of the potentials rather than their absolute values of the redox e.m.f. near the ore bodies.

Simultaneously several authors (Latimer, 1938; Zobell, 1946; Krumbein and Garrels, 1952; Garrels, 1954; Baas Becking et al., 1960; Sato, 1960) have contributed significantly on the redox phenomena in the earth's natural environment and improved the techniques of redox potential measurements. They have outlined the practical difficulties in measurements of redox potentials in natural environments and indicated that the absolute values of the redox potentials are not reproducible even with precision measurements. As a result quite a few workers have given up the idea of redox measurements since the absolute values of the non-reproducible potentials did not make any sense to them.

Concurrently the existence of borehole S.P., which can be of use in delineating porous and permeable beds and are of diffusion and diffusion-adsorption origin, was first detected by Schlumberger et al. (1934). Since then may authors (e.g. Doll, 1948; Gondouin et al., 1957) have established the S.P. logging as a regular tool for borehole geophysics. On the contrary, the borehole S.P. of redox origin in the sedimentary, igneous and metamorphic mineralized zones remained fairly unattended till 1958 when G.B. Salimbeni carried out his first redox logging in pyrite, lignite and oil wells of central Italy. Since then a large number of workers have contributed significantly in the understanding of the behaviour of redox logs in mineral and oil wells (e.g. Colombo et al., 1959; Pirson, 1968, 1970; Karaoguz et al., 1970). The theories of redox potentials are discussed in detail by Zobell (1946), Glasstone (1962, 1969), Garrels (1970), and Pirson (1968, 1970). The different techniques of redox logging are reported by Colombo et al. (1959), Pirson (1970), Karaoguz (1970).

The present authors started model experiments keeping in view firstly the possibilities of enhancing the redox anomalies by changing the pH of the drilling

fluids instead of adding any oxidizing or reducing agents and secondly to study the effect of concentration of mineral grains on redox anomaly. The results of our experience are enumerated in the following sections.

2. Experimental Set-up, Measurements and Discussion of the Results

A. Standardization of the Measuring Probes

Before trying to measure the potentials of unknown systems, we tried to standar-dize our electrodes (Platinum-Calomel) by inserting them in a Zobell solution and measuring the potentials in an accurate (± 10 micro volts) potentiometer. The standard techniques of potentiometric measurements are well known and therefore are omitted here. We could measure 0.35209 gms of $K_4Fe(CN)_6$ $3H_2O$ and 0.311130 gms of $K_3Fe(CN)_6$ $3H_2O$ whereas the theoretically required weights to prepare solutions of strength M/300 in 250 cc of distilled water are 0.35200 gms and 0.311100 gms respectively.

25 cc of each of M/300 $K_4Fe(CN)_6$ $3H_2O$, M/300 $K_3Fe(CN)_6$ $3H_2O$ and M/10 KCL are taken in a beaker and the potentials are measured (Fig. 1) with platinum-calomel electrodes. The value is found to be 175 mV at 86° F or 30° C. Hence Eh $= 175 + 245 = 420$ mV at 30° C or 423 mV at 25° C. The correct value should be 428 mV as reported by Zobell (1946).

In the same solution the Pt-Pb electrode is immersed and the stable potential observed was 512 mV. In other words the level of Pt-Pb potential is found to be at 347 mV above that of (Pt-Cal) potential.

B. Effect of Concentration of Mineral Grains on Redox Potential

Samples of various ores were collected from different field sites[1] of India. The ore samples are crushed to make powders and are mixed with plaster of paris in different percentage by weight. Cylindrical casts of plaster of paris are then prepared with holes in the centres (Fig. 2). 10 gms of hematite ore in 100 gms of plaster of paris makes a sample of 10% hematite.

The central hole of the model is plugged by rubber stopper at the bottom (Fig. 2) and solutions of certain pH value are poured in steps till the pore spaces in the cast are saturated with the solutions and the solution remains in the hole without any infiltration loss. The cast is left as such for about half an hour in this form and then the potential is measured in the hole with Pt-Cal and Pt-Pb electrodes (Fig. 2). When the measurements are made with the Pt-Cal electrodes, the Calomel electrode is placed in the 10% KCL bath

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[1] 1. Hematite (Kiruburu, Singhbhum, Bihar, 98% hematite); 2. Pyrite (Amjhor, Sasaram, Bihar, 50% Pyrite); 3. Chalcopyrite (Mosabani, Singhbhum, Bihar, 10% Chalcopyrite, It was present in the disseminated form); 4. Galena (Zawar, Rajasthan, 20% Galena; It was also present in the disseminated form); 5. Bauxite (Lohardaga, Singhbhum, Bihar, 60% Bauxite); 6. Graphite (Athmallik, Dhenkanol, Orissa, 90% Graphite); 7. Bituminous Coal (Ranigang, West Bengal); 8. Lateritic surface clays (Kharagpur, West Bengal)
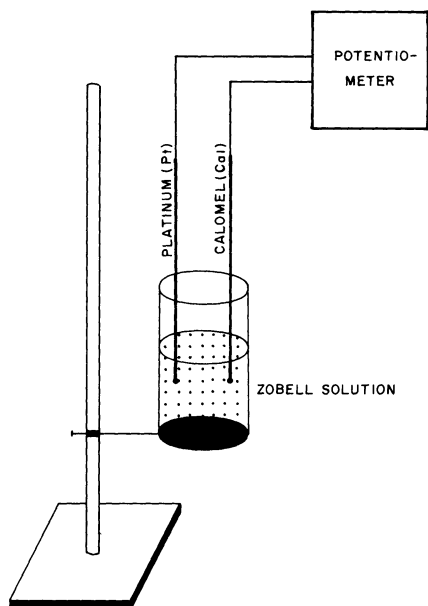
Fig. 1. Standardization of electrodes in Zobell solution
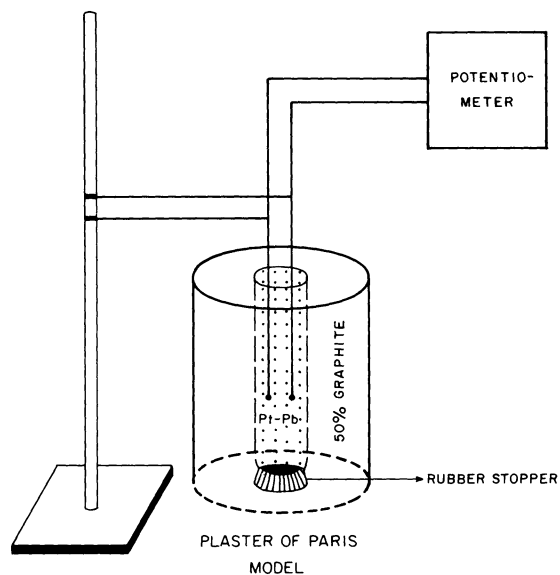

Fig. 2. Redox potential measurement in the plaster of paris model

and the connection with the plaster of paris cast is made by an agar-agar bridge. A similar type of set up is shown in Figure 3.

We have taken about 700 observations in hematite and 400 observations each in graphite, chalcopyrite, and bauxite. The results of our investigations are summerized as follows:
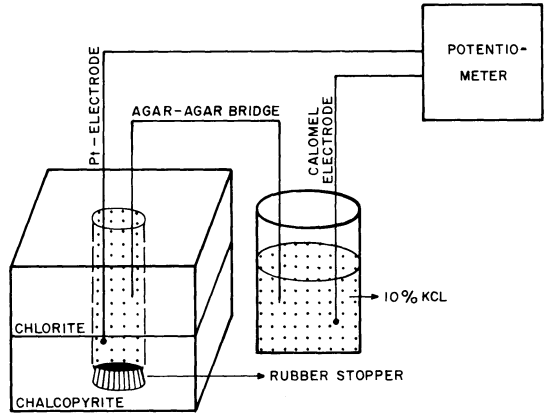
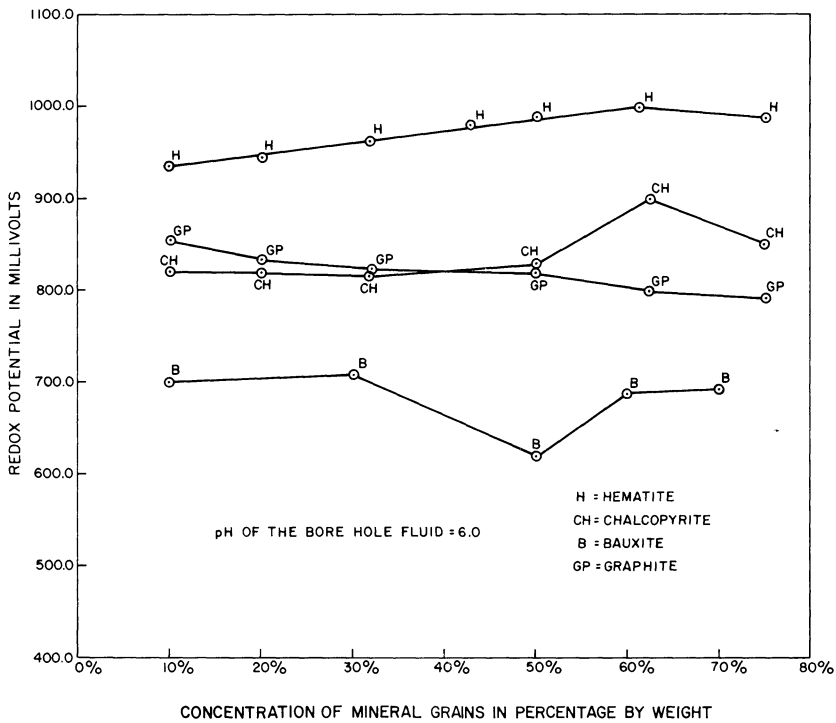**Fig. 3.** Redox potential measurement with Pt-Cal electrodes using agar-agar bridge across chlorite-chalcopyrite block

Fig. 4. Effect of mineral concentrations in the plaster of paris models on redox potential (pH = 6.0)

(a) The potential takes about 10 min − 2 h before it gets stable within a limited time span of 30 min − 60 min.

(b) When the measurements are repeated after a long time gap of 16 − 20 h, a significant change in the potential, of the order of 200 mV, is observed.

(c) For every cleaning operation of the platinum electrode a sudden jump in the potential is observed. Therefore we decided to clean the platinum electrode

at the beginning of each observation and chose the value as our reading when it remained more or less stable within a time span of half an hour.

(d) The potential is found to be almost independent of concentration of the minerals in percentage by weight when the observations are taken with tap water (pH = 6.0) and also with alkaline electrolytes (pH = 7.0 to 12.0) (Fig. 4). However, some distinct trends of variations of potentials are observed when acidic electrolytes are used for measurements. Observations with pH = 0.5 are presented in Figure 5. Almost similar type of trends are observed when solutions of pH = 1.0 and 2.0 are used. It appears that the sensitivity of the redox anomaly may increase with gradual decrease in the pH of the borehole fluid.

(e) Although the level difference between Pt-Pb and Pt-Cal electrode in the Zobell solution was found to be 347 mV, the level differences in the plaster of paris model for hematite are found to be slightly on the higher side, i.e., about 430 mV on an average. Similar results are obtained with other models also.

C. Potential Difference across Natural Field Samples

Chalcopyrite and chlorite samples were collected from the Mosabani field. The samples are trimmed to make rectangular blocks and they are attached to one another by araldite (fixer) to make a leak proof block. The field geologic successions are maintained in the model (Fig. 3). A hole (diameter 2 cm) was drilled through the middle of this block. Tap water was poured through the hole and the water was allowed to stay for 3 days before the redox logs were taken with Pt-Pt and Pt-Cal electrodes using the agar-agar bridge.

Remarkable difference in the redox potentials across the chlorite chalcopyrite blocks are observed when the observations are repeated in 4 consecutive days (Figs. 6 and 7). Although the absolute values could not be reproduced, the trends of variations remained more or less the same. This experiment has given us the idea of investigating the variations of the redox potentials, rather than their absolute values, in the laboratory models.

D. Model Tank Experiment

A semi-cylindrical model tank, height 51.5 cm and radius 30 cm with a front transparent face of 61 cm × 51.5 cm, was prepared in the laboratory. Alternate layers of lateritic surface clays and ores are simulated in the tank as shown in Figure 8. A borehole in the model tank was simulated by holding a wooden rod vertically during the packing of the tanks with clays and ores. Afterwards the rod is taken out from the tank and a borehole is made through the entire cross section of the clay/ore/clay. The model tank is constructed over a bakelite base. A small hole is drilled below the borehole such that the borehole fluid can be changed from time to time. Platinum − lead electrodes are used for measurement of potentials keeping the Pt-electrode at the top of the borehole
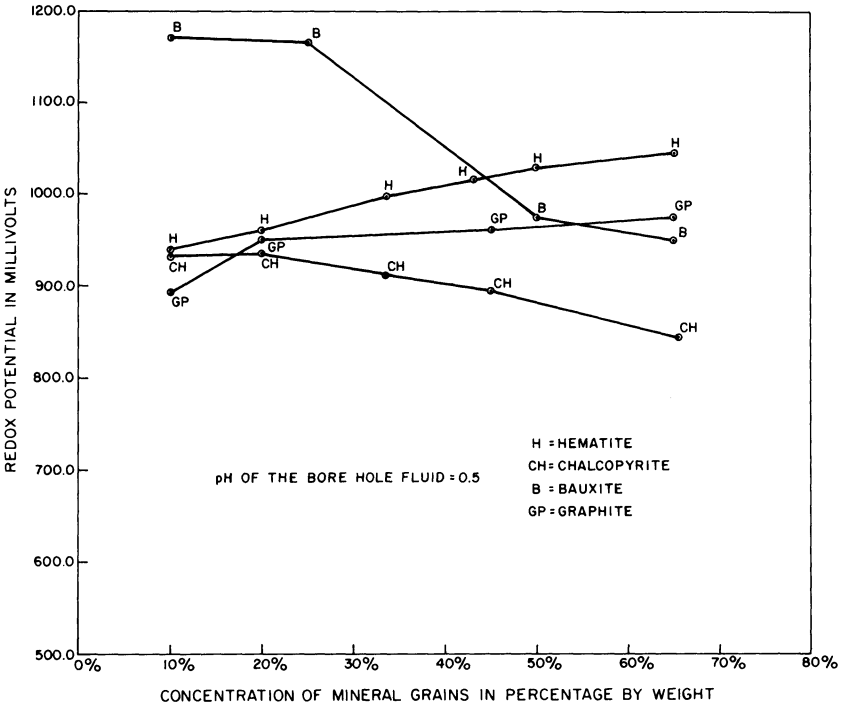
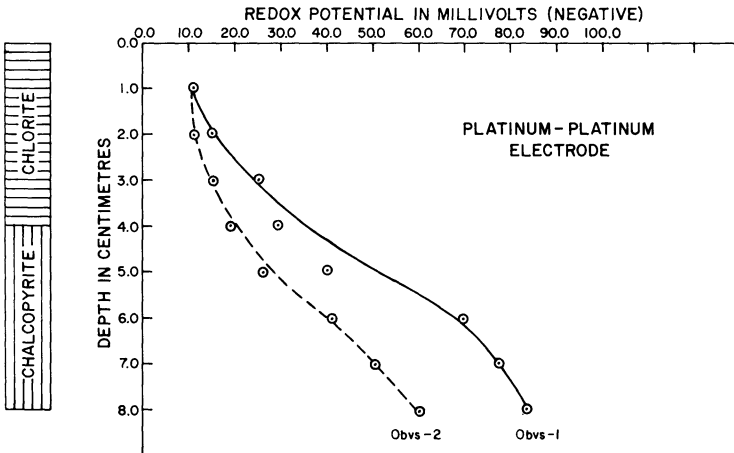**Fig. 5.** Effect of mineral concentration in the plaster of paris models on redox potential (pH = 0.5)

Fig. 6. Redox log across chlorite-chalcopyrite block with Pt-Pt electrodes (borehole fluid — tap water)
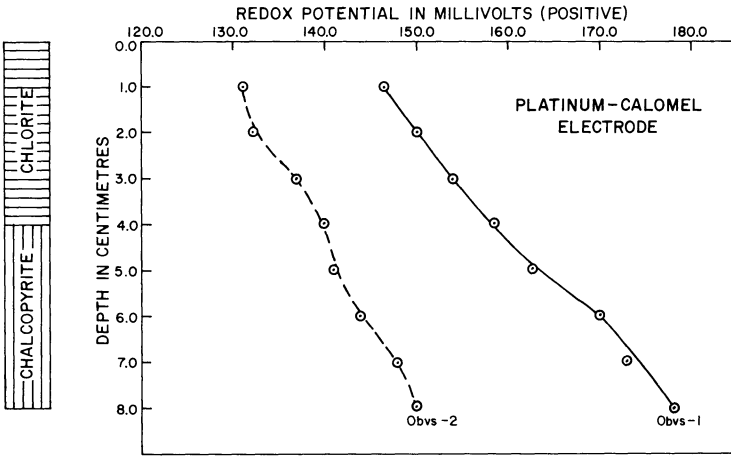
Fig. 7. Redox log across chlorite-chalcopyrite block with Pt-Cal electrodes (borehole fluid — tap water)
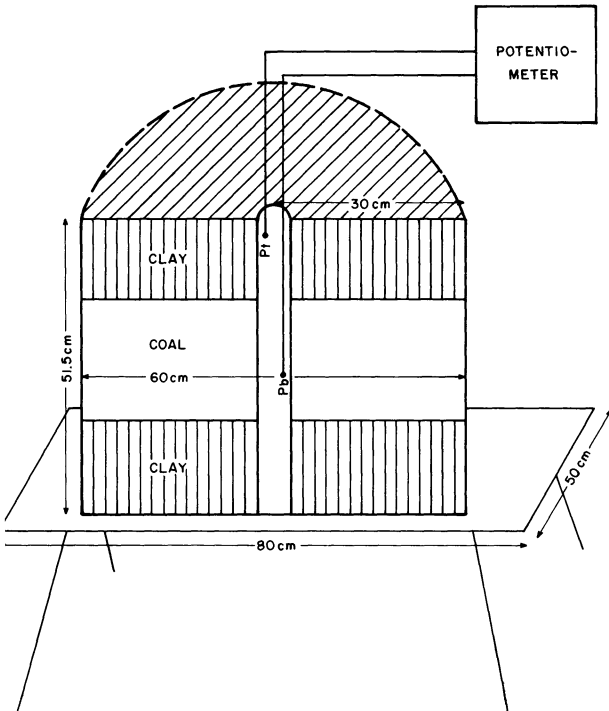

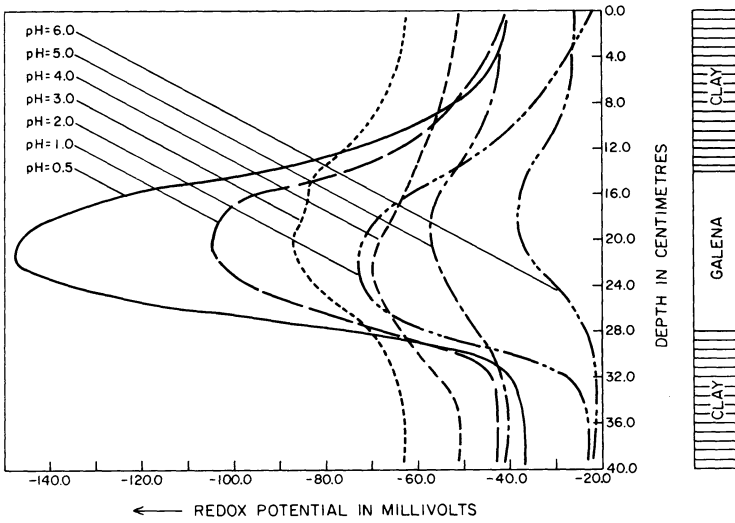**Fig. 8.** Model tank for redox potential measurements inside a simulated borehole

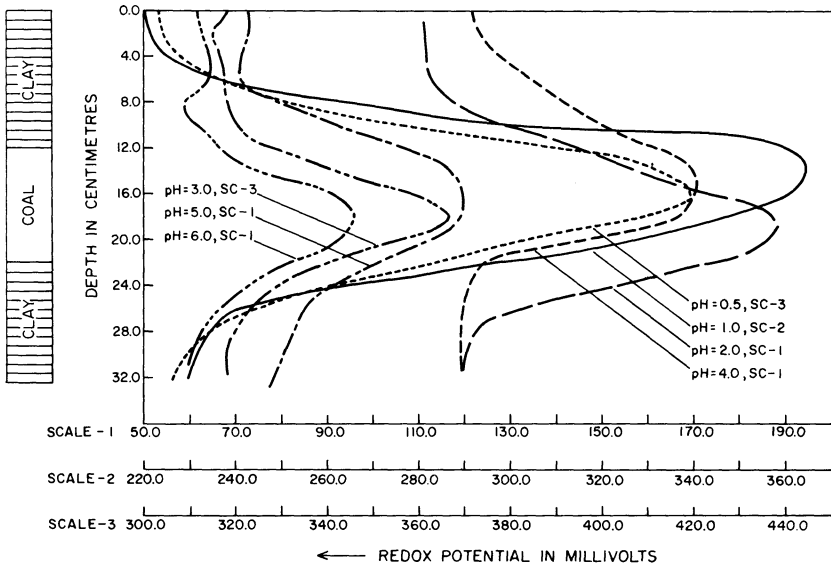**Fig. 9.** Redox log across clay/galena/clay with Pt-Pb electrodes

Fig. 10. Redox log across clay/coal/clay with Pt-Pb electrodes

and allowing the Pb electrode to move through the entire cross section. The fluids of different pH are inserted in the borehole and the observations are repeated. The results are presented in Figures 9, 10, 11 and 12. In order to economize space only a few curves are presented. However, the results are summarized in Figure 12. They reveal the following facts:
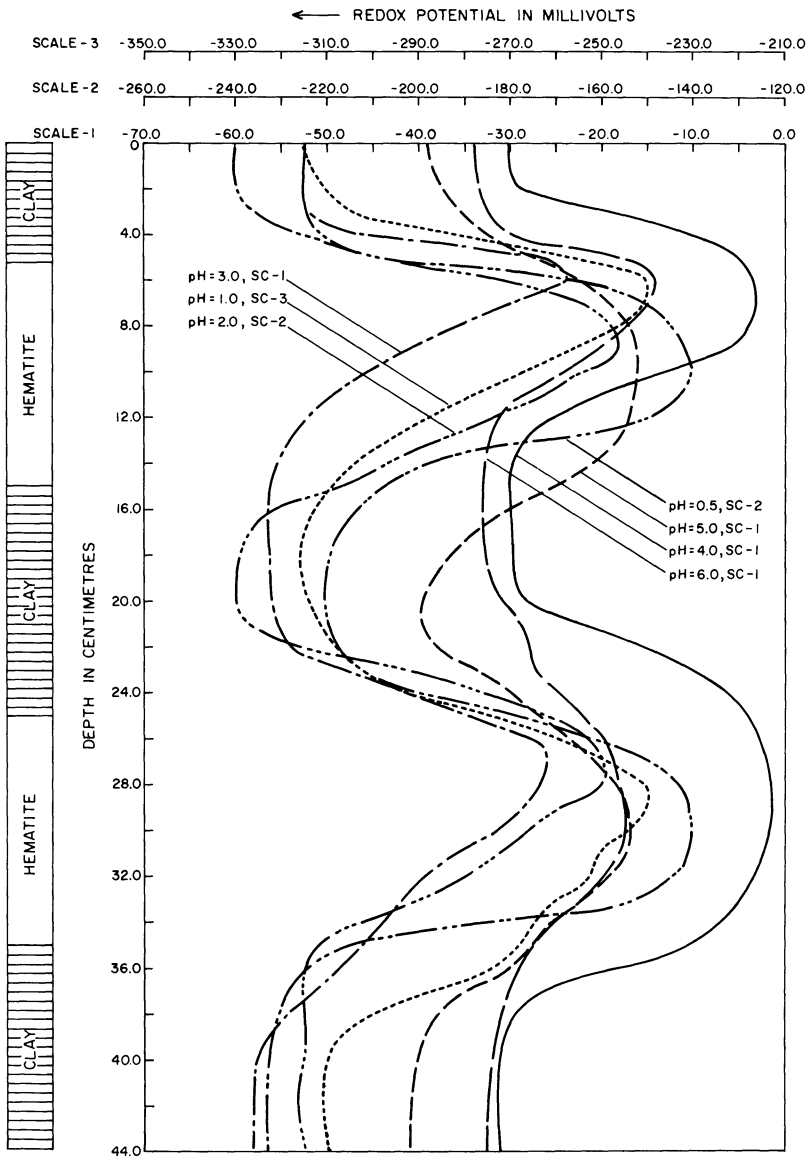
Fig. 11. Redox log across clay/hematite/clay/hematite/clay with Pt-Pb electrodes

    1. The redox logging is good enough to detect the depths and approximate thicknesses of the ore bodies.

    2. The absolute values of the potentials are not reproducible and therefore these values cannot be used for any quantitative interpretation.

    3. The redox anomaly is found to become sharper and sharper with the increasing acidity of the borehole fluids.
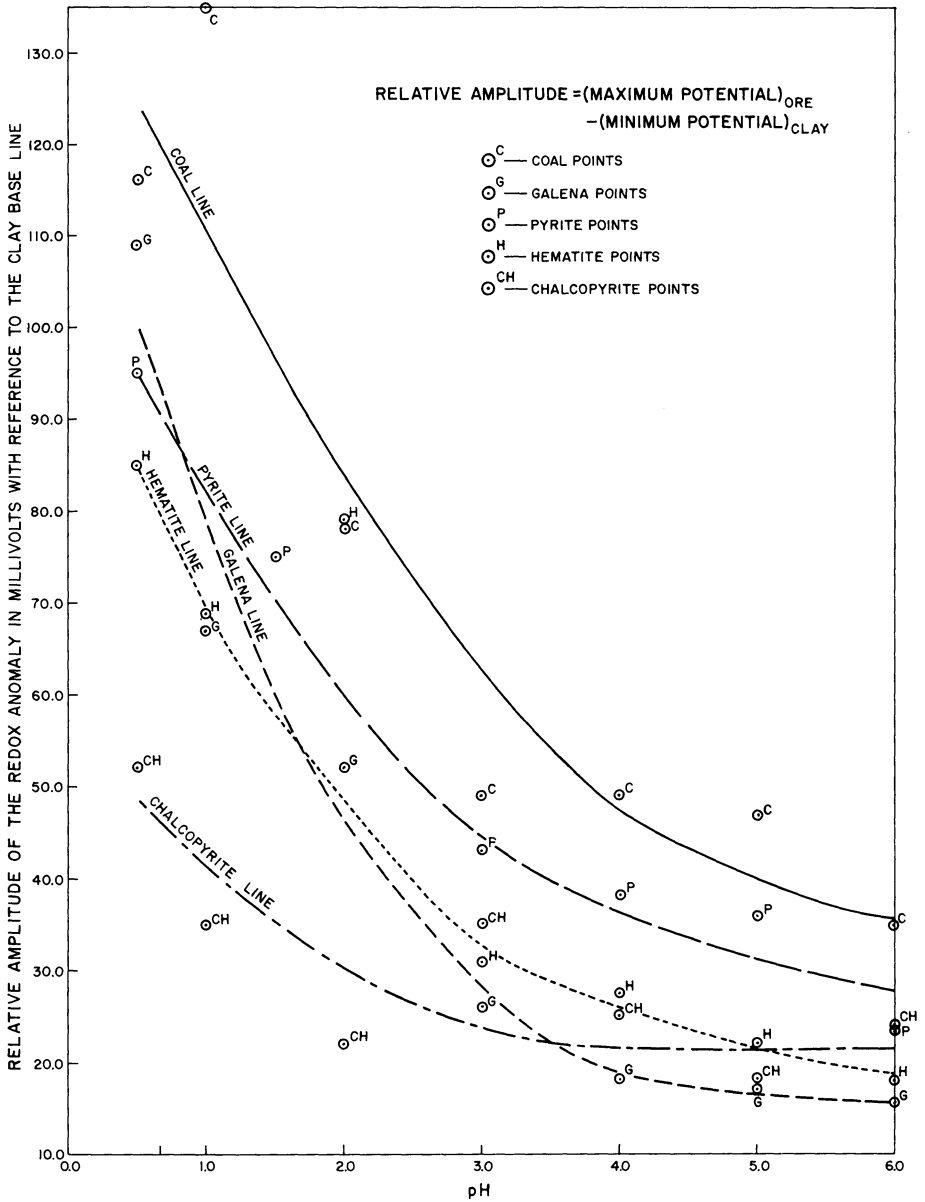
Fig. 12. Variations of redox anomalies with pH

4. Like other geophysical methods viz. gravity and magnetic methods, the relative change of the redox potential rather than their absolute values will be of more interest to the geophysicists.

5. The change in potential per unit change in pH is found to differ widely for different minerals.

The present set of data shows how the signals become prominent surpassing

the high noise levels in redox measurement. These data are presented largely as a qualitative measure and no attempt is made to go for any quantitative analysis, since the data could not be made reproducible within 5% in all cases. Sometimes the variations are significant. The instrumental complications in redox measurements are minimum. All we need are (i) a pair of Pt-Pb or Pt-Ag AgCl electrodes (ii) one reel of two core cable and (iii) a potentiometer.

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