CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 65-95

APPLICATION OF POTENTIOMETRIC TITRATION TO THE STUDY OF SURFACE ELECTRIC PHENOMENA

by

N. NEMETH, L. L. SIROIS & T. TAKAMORI

MINERAL PROCESSING DIVISION

COPY NO. 24

NOVEMBER 19, 1965

Mines Branch Investigation Report IR 65-95

APPLICATION OF POTENTIOMETRIC TITRATION
TO THE STUDY OF SURFACE ELECTRIC
PHENOMENA

by

N. Nemeth* - L. L. Sirois** - T. Takamori***

- - - -

SUMMARY OF RESULTS

A simple experimental technique for the determination of zero points of charge of minerals by potentiometric titration, is described and illustrated by actual test data for silica, magnetite and asbestos.

*Scientific Officer, **Senior Scientific Officer, Head, Metallic Minerals Research Laboratory, Mineral Processing Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada. ***National Research Council Fellow.

FIGURES

TABLES

INTRODUCTION

The study of flotation chemistry is basically a study of the electro-chemical phenomena which occur between a solid surface and a solution. The theoretical aspects of the surface electrical phenomena of minerals are treated in great details in the literature (1, 2, 3). A brief summary of this theory will be presented here. This report is intended, mainly, to describe the method and application of potentiometric titration in the determination of the zero point of charge of various mineral surfaces such as quartz,. magnetite and chrysotile.

The information obtained for chrysotile will be presented in greater details in another paper as this was part of a general study on the properties of asbestos.

Outline of Theory

A flotation system has three components, a liquid phase or electrolyte; a solid phase, the finely divided mineral particles; and a gaseous phase, introduced as bubbles into the pulp. The success of a flotation operation depends to a large extent upon the interaction of the liquid and solid systems. Thus the nature and the structure of the interface existing between the solid and solution phases are important elements in flotation.

At solid-liquid contacts, charged ionic species will be transferred. This ionic transfer is either due to the dissociation of the solid with resulting passage of ions to solution and/or the uptake of ions by the solid from the solution to satisfy charged or "active" sites on the surface. The origin of surface charges of broken mineral surfaces has been explained by Gaudin and Fuerstenau. Potential determining ions determine the sign of the surface charge of a solid. They are unique for each solid. In the case of ionic solids, they are the ions constituting the crystal lattice. In the case of many insoluble oxide minerals, H^+ and OH^- are the potential determining ions, as for quartz, magnetite, and cassiterite.

There are two opposing forces that govern the transfer of ions across the liquid-solid interface. One of them is the chemical potential that represents chemical work gained by the charge transfer and this equals the second force, the electrical work that will be spent removing a positive charge from a negative surface and placing it in a positive phase, or vice versa.

The equilibrium state between the phases is described by the following equation: (2)

$$(\mu_+^{solid} - \mu_+^{solution}) = Z_i + e_o (\psi^{solution} - \psi^{solid}) \quad \text{(Eq 1)}$$

which states that at equilibrium, the chemical potential difference of the two phases equals the created electro-chemical potential. The terms are:

μ = chemical potential

Z_i = Valence of charged species

e_o = charge of an electron

$\psi^{solution} - \psi^{solid}$ = an electrostatic potential difference due to a transfer of electrons.

From this previous equation, a rearrangement of terms yields:

$$\mu_+^{solid} + Z_i + e_o \psi^{solid} = \mu_+^{solution} + Z + e_o \psi^{solution} \quad \text{(Eq 2)}$$

and finally:

$$\bar{\mu}_+^{solid} = \bar{\mu}_+^{solution} \quad \text{(Eq 3)}$$

where each side of equation now represents the "Electro-chemical" potential of each phase. Thus it is possible to relate the changes in the potential difference to the activity (or concentration) of the solute in the solution phase (2).

The interaction between a charged solid surface and an aqueous solution leads to the development of the electrical double layer. A simple illustration of this phenomenon occurs, for example, with silica in water, where negative charges are fixed on the mineral surface and the solution phase has an increased positive charge density in the immediate vicinity of the surface. This excess charge will degrade with distance from the surface, and at the same time it will give rise to diffusion currents in the solution, that will attempt to minimize this ionic concentration near the solid surface.

When a surface acquires its charge by obtaining ions from the solution, the process is mainly controlled by the activity, in the solution, of the species in question. Consequently, there must be a concentration at which all forces are in equilibrium and the total net transfer of ions becomes zero. When this situation occurs, there will be no excess charge on the surface and consequently no cause for the existance of an electrical double layer.

The zero point of charge will occur when this electrical double layer is absent and the surface of the solid shows no excess positive or negative charge due to the presence of excess electrons or cations. It is thus determined by the critical concentration or the activity of the potential determining ions in the solution.

The potential that is developed across a double layer is expressed by the equation:

$$\psi_o = \frac{RT}{Z_i F} \ln \frac{a_i}{a_{io}} \qquad (Eq\ 4)$$

At the zero point of charge this potential will be zero. However, it is important to remember that the total potential difference between the two phases is not zero. A certain potential difference will exist due to some polarization of water molecules. The double layer created by the water dipoles surrounding the solid particles does not involve a transfer of electrons.

Flotation is a process where the attachment of the collector ions is greatly dependent upon surface electrical characteristics and the resulting double layer. In flotation systems there will be more than one potential determining ion. For base metals the metallic cation or the sulphide ion may be considered as potential determining, as well as the OH^- and H^+ ions. The OH^- and H^+ ions are the most important potential determining ions for oxide minerals as well.

The adsorption of H^+ and OH^- ions can be found by carrying out potentiometric titrations. The end point in this neutralization titration is found by direct measurement of the pH of the solution after each addition of an alkali or an acid. The pH - neutralization curve is followed experimentally and the equivalence point determined. The difference

between the titration curve with the mineral present and the one provided by a control experiment in which no mineral is introduced determines the amount of charge developed on the surface by ionization or adsorption of H^+ and OH^- ions.

EXPERIMENTAL DETAILS

(1) Equipment

The basic component of this apparatus is a glass cell of approximately 500-600 ml volume. This cell has a suitable inlet near its lower part to allow introduction and mixing of an inert gas. The cell must have a large opening at the top to accommodate a stopper through which the following items can be inserted:

(i) glass and calomel electrodes
(ii) thermo-compensator for the pH meter
(iii) burette for acid/base additions
(iv) small outlet for gas
(v) seal containing the shaft of a mixer

A cylindrical pyrex glass vessel of approximately 4" diameter was found to be satisfactory. The assembled cell is illustrated in Figure 1. As it is often impractical to use a magnetic stirrer, a mechanical mixer must be used. Both are represented in the diagram but only one would be used at a time. The insertion of a mechanical stirrer presents some difficulties in a sealed cell. A special mercury seal was designed and is shown in Figure 2.

The titration process lasts for several hours and it is possible that there is a grinding effect on the solids when the magnetic stirrer is used. For this reason a mechanical stirrer may be more appropriate. However, the application of a mechanical stirrer has disadvantages unless the special seal arrangement shown in Figure 2 is used.
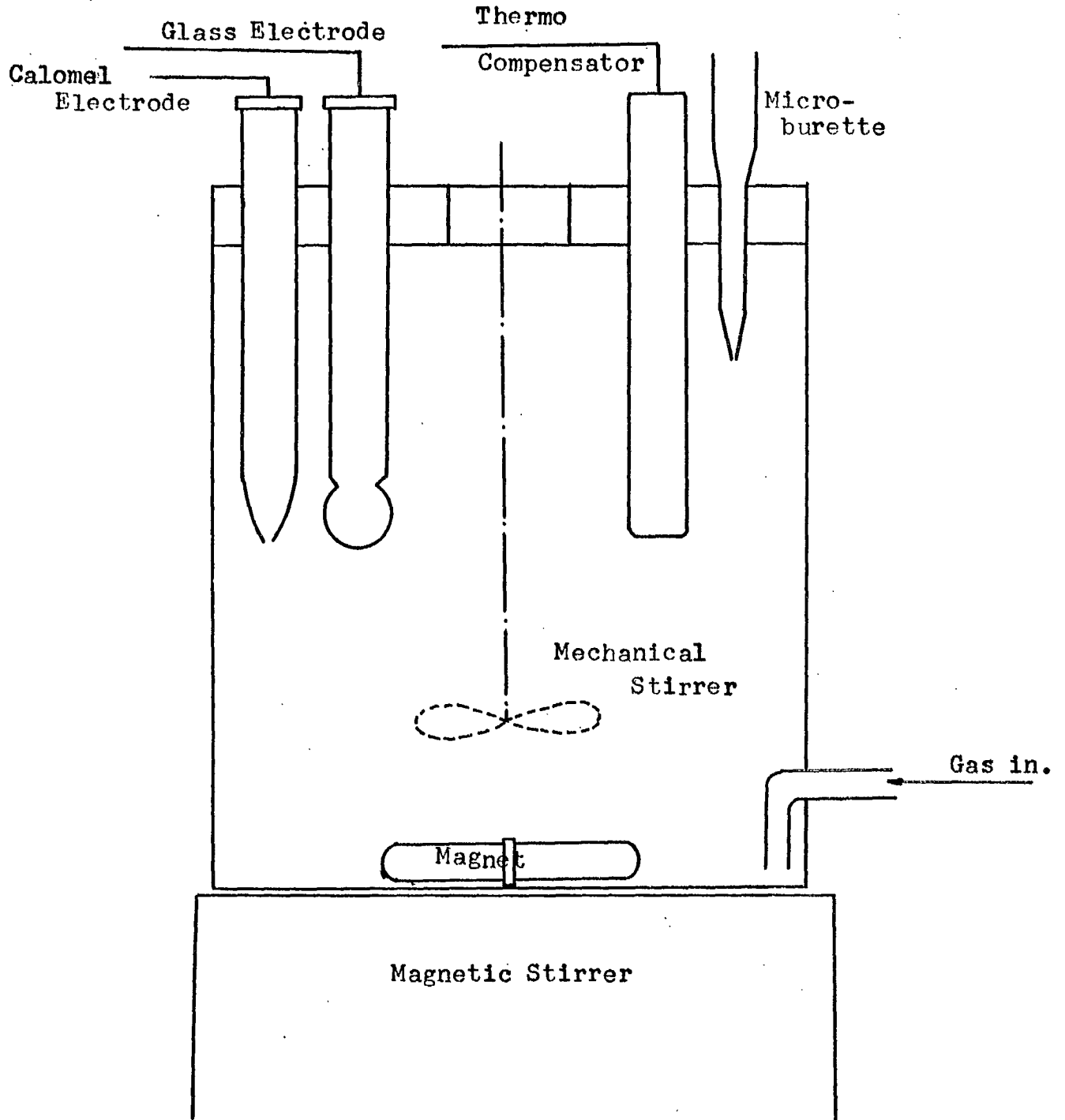
Figure 1: General Layout of the Potentiometric Titration Apparatus
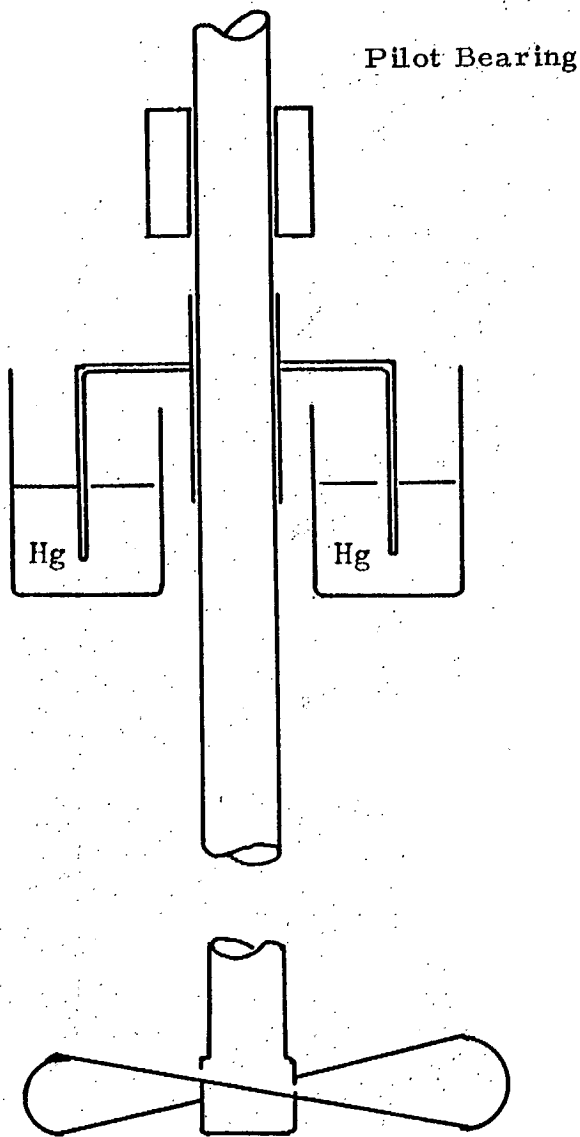
Pilot Bearing

Hg Hg

Figure 2: The Mercury Seal for the
Mechanical Mixer

Abrasion was observed with a brass bearing. Even although extreme care was used, it is possible that some of the fine brass powder contaminated the solution when the mercury seal was not used.

An aqueous system such as the one used for potentiometric titration can be influenced by the CO_2 content of the atmosphere. Therefore, an inert gas, either nitrogen or argon, is used to provide an inert atmosphere in the cell, above the solution. Very often the purity of the commercially available gas is inadequate. In these experiments a purifying train was used to remove most of the impurities from the gas. The following were part of the purifying train:

     (i)   10% NaOH solution
     (ii) 10% HCl solution
     (iii) distilled water
     (iv) bottle filled with glass wool

To control and protect the system from contamination by acid vapours, the distilled water was checked for pH frequently and changed if necessary. For very accurate results the cell should be immersed in a constant temperature bath.

Other parts of the equipment were:

     (i)   a Beckman Zeromatic pH meter with an accuracy
         of $\pm$ 0.1.
     (ii) a special abrasion resistant Metrohm glass electrode.
     (iii) a microburette of 0.05 ml accuracy.

Since this titration method is basically an adsorption process it is recorded as a concentration change of the H^+ ions in the solution. Therefore, a great improvement was achieved by employing an automatic recorder in conjunction with the pH meter. This produced a graph of the continuous pH change with good visual appreciation of the end point for each addition of acid or base.

(2) <u>Test Procedure</u>

     (1) <u>Size and preparation of the samples.</u>

Samples should range in size from 2 to 10 grams. This weight

depends mainly on the fineness and thus on the surface area of the mineral in question. The total volume of the system should be approximately 400-500 ml. In preparing a mineral, surface purity is most important. The samples were cleaned by numerous washings and decantation whereby the -10 sizes were removed. Exposure of the dry samples to the atmosphere can alter their surface characteristics significantly so after cleaning the samples were kept under water.

(2) Titration without the solids

500 ml of an aqueous solution of an indifferent electrolyte, such as KCl solution, is titrated with an acid ($HClO_4$) or a base (KOH). The concentration of the electrolyte, the acid and the base are accurately determined. The titration yields a relationship between the pH of the system and the volume of acid or base added. Small additions are made to obtain a well-defined curve which is plotted as shown in Figure 3.

(3) Titration with the solids

To an identical 500 ml volume and concentration of the electrolyte, the mineral sample of known weight is added. From an initial point - the equilibrium point between the electrolyte and the solid - acid titration is made as in (2) preceding and plotted. Similarly, with an identical sample, the basic potentiometric curve is obtained.

The new curve represents the relationship between the pH of a system with suspended solids in it and the volume of acid or base added. By superimposing the two curves of (2) and (3) as in Figure 3 the differences in volumes can be obtained by measurement at a series of pH values. These indicate the equivalent volumes adsorbed by the solids suspended in the electrolyte.

(4) Specific surface area of solids

The specific surface area of the solids must be determined by some accurate method.

The volume of acid or base of a certain concentration will be equivalent to a number of negative and positive ions. It is assumed that the acid $HClO_4$ and KOH will be completely dissociated in a 0.1N aqueous solution. Thus, from this volume the number of H^+ ions or OH^- ions can be calculated (4). With such information the final expression of the surface electrical parameter:

$$\frac{No.\ of\ ions}{cm^2\ of\ mineral\ surface}$$

can be obtained.

RESULTS AND DISCUSSION

Results of the potentiometric titrations are
summarized in Table 1

TABLE 1

pH Values for ZPC of Minerals at Various
Electrolyte Strengths

Minerals	Ionic Strengths of KCl Electrolyte				
	0.1	1×10^{-2}	6.71×10^{-2}	6.71×10^{-3}	6.71×10^{-4}
Magnetite		5.8		5.75	5.7
Quartz	2.4		2.5	2.6	
Chrysotile		10.8			10.6

Results for Quartz

The specific surface area of the quartz sample was determined
as 1130 cm²/g.

Figure 3 shows two adsorption curves, one with and one without
quartz, with 0.1N HClO$_4$ solution. The ionic strength of the supporting
electrolyte (KCl) solution was 6.7×10^{-4}. Two other tests not shown on
Figure 3 were also carried out with 0.1N HClO$_4$ solutions at 0.1 and
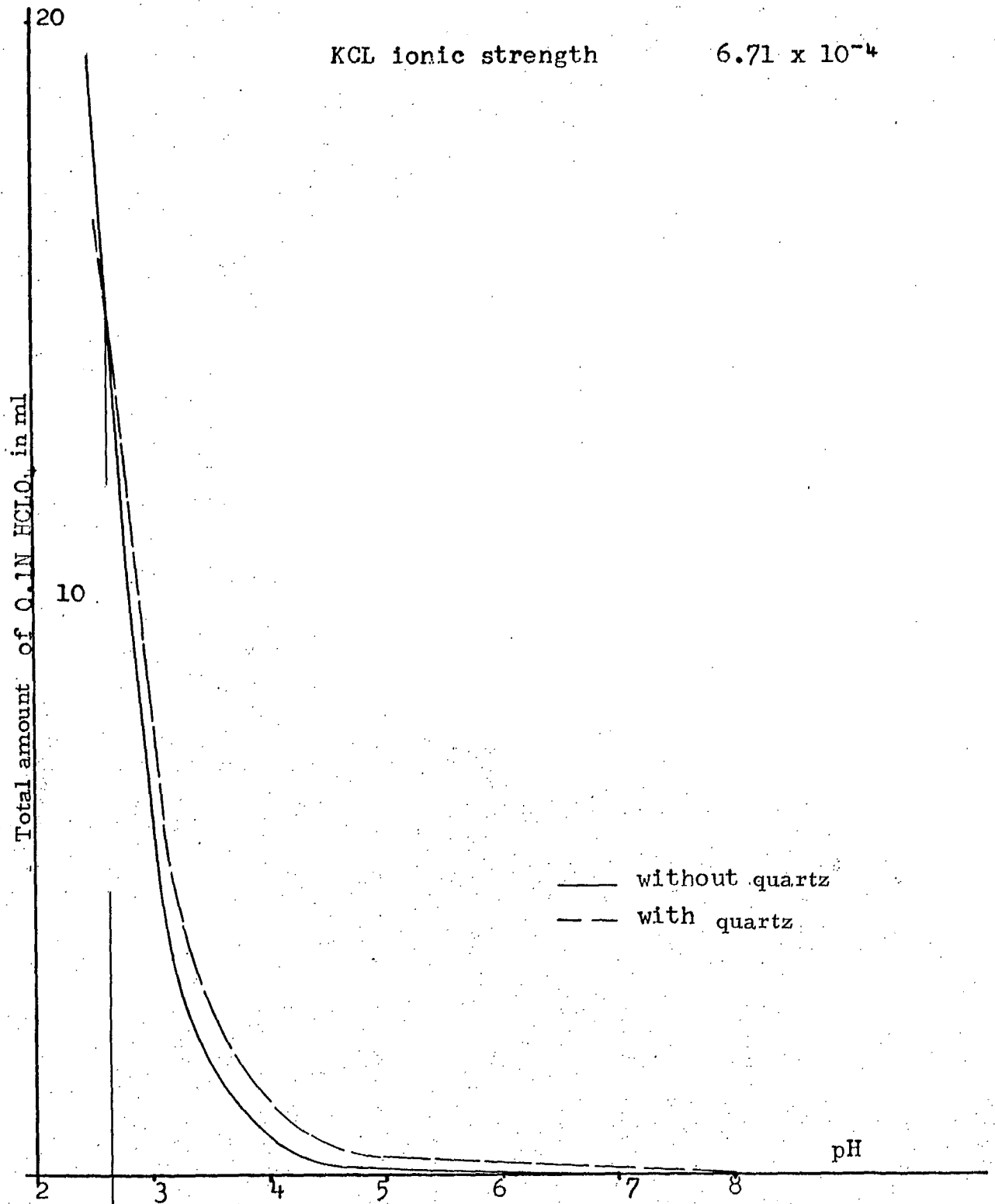6.71×10^{-2} KCl electrolyte concentrations.

Figure 3: pH Variation of the KCl Electrolyte
Solution with and without SiO_2

TABLE 2

Acid Adsorption Differential at Each pH Value for Quartz
(ml of 0.1N $HClO_4$)

	Ionic Strength of KCl Sol'ns		
	0.1	6.71×10^{-2}	6.71×10^{-4}
pH	0.1N $HClO_4$ ml	0.1N $HClO_4$ ml	0.1N $HClO_4$ ml
2.4	Z P.C		
2.5	1.6	Z P C	
2.6	2.3	1.5	Z P C
2.7		1.8	
2.8	2.8	2.0	0.6
2.9	2.9		0.8
3.0	2.6	2.1	1.0
3.1	2.4	2.0	1.2
3.2	2.3	2.0	1.3
3.3			1.4
3.5	2.0	1.7	1.1
3.7	1.8	1.5	0.7
3.8			0.6
3.9		1.3	
4.0	1.5		0.5
4.2		0.8	

Sample Weight   :   45g
Specific Surface :   1130 cm^2/g

From Figure 3, the adsorption differentials, at various pH values, can be measured as tabulated in Table 2. The amounts of acid adsorbed correspond to the H^+ ions that were picked up by the negatively charged SiO_2 surface to satisfy unbalanced surface charges. At each pH value this is equivalent to the number of active sites on the silica. At the intersection of the two curves the acid adsorption differential becomes zero and the zero point of charge occurs at this characteristic pH value. The ZPC values for silica occur at pH 2.4; 2.5 and 2.6 for the three different electrolyte concentrations. The accuracy of the Beckman Zeromatic pH meter used is 0.1.

The plotted results in Figure 4 illustrate the effect of the variation of active sites with pH. These curves intersect the horizontal axis at a pH value characteristic of the zero point of charge of the mineral. This point occurs at a very low pH value for strongly acidic oxides; with increasing pH the surface becomes more and more negative, due to the loss of H^+ ions to the solution and finally dissolves at high pH values.

Magnetite

An identical method was followed in the determination of the zero point of charge of magnetite. The specific surface area of the sample was 1970 cm^2/g. The solution concentration for both acid and base was 0.01 N. Again three ionic concentrations of the KCl electrolyte were used. The adsorption differentials, for the three electrolyte concentrations, are tabulated in Table 3.

In Figure 5 the final curves are plotted for magnetite showing the volume adsorbed versus pH relationship. Magnetite, being an amphoteric oxide, should have its zero point of charge in the near neutral pH range. Hence it was necessary in this case to cover both the basic and acidic sides in titration as shown in Figure 5. Although the absolute amount of ions adsorbed is different at various KCl - electrolyte concentrations, the pH value representing the actual zero point of charge is very closely duplicated. Thus a multiple assurance for its location is obtained.

The following pH values were obtained for the zero point of charge of magnetite: 5.7, 5.75 and 5.8 which is again well within the accuracy of the instrument.
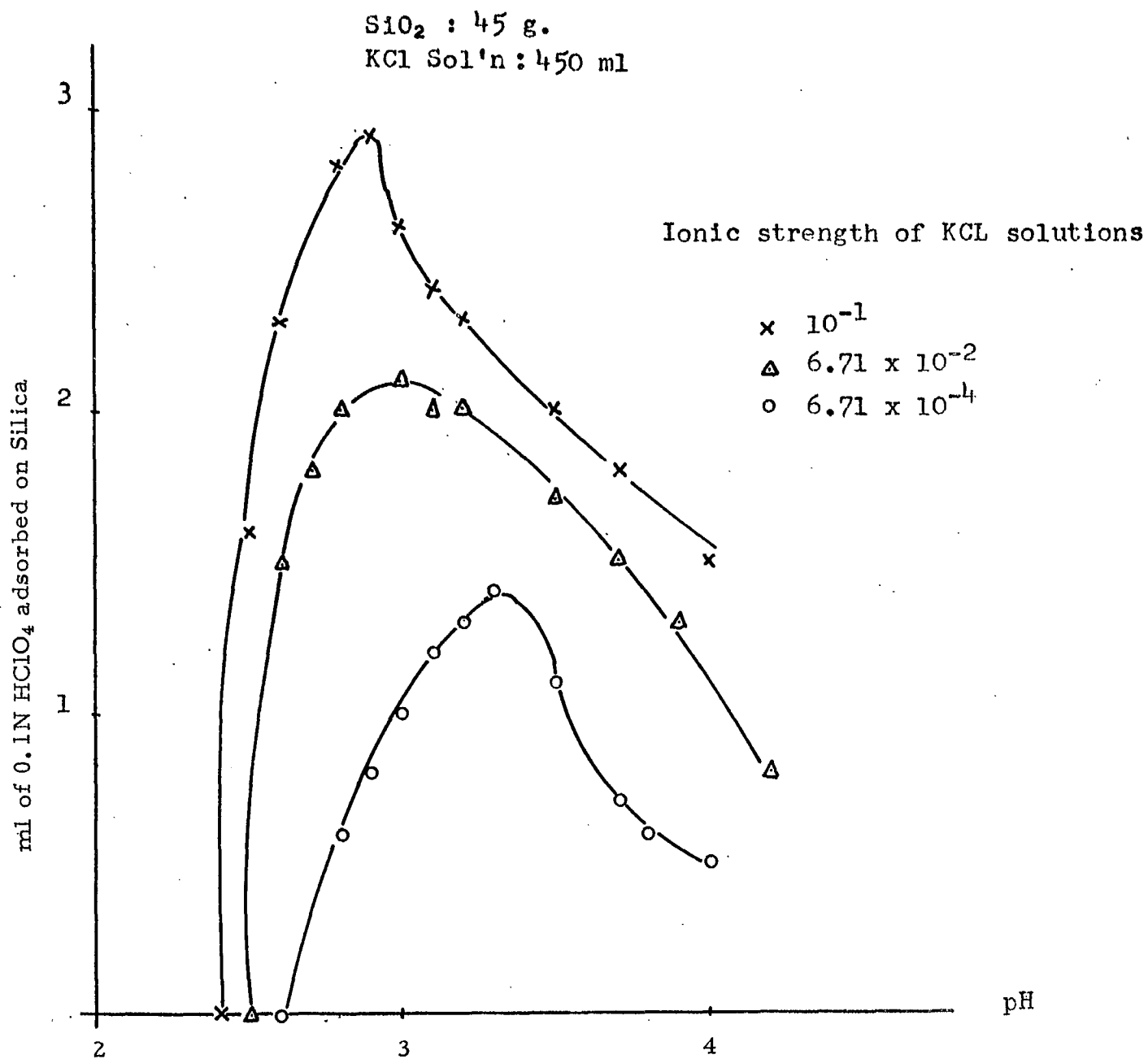
Figure 4: Potentiometric Titration
of Silica

Asbestos

The asbestos mineral chrysotile is very complex and it is not without provoking an argument that one can say that its Z P. C was found at pH 10.7. There can be a number of processes or surface reactions that may occur simultaneously with asbestos in aqueous solutions. One of them would likely be ion exchange. At the assumed zero point of charge, therefore, there would exist a complex equilibrium which would be very hard to describe quantitatively.

TABLE 3

Adsorption Differentials For Magnetite

pH	Ionic Strength of KCl Solutions					
	10^{-2}		6.7×10^{-3}		6.71×10^{-4}	
	0.01N HClO$_4$ ml	0.01N KOH ml	0.01N HClO$_4$ ml	0.01N KOH ml	0.01N HClO$_4$ ml	0.01N KOH ml
5.0	6.8				5.5	
5.2					2.4	
5.3			2.5			
5.4			1.2		0.8	
5.5	1.4					
5.7					Z P C.	
5.75			Z P C			
5.8	Z P C					
6.0		0.5		0.4		
6.04						0.4
6.5		3.5		2.4		1.8
7.0		6.5		5.2		3.7

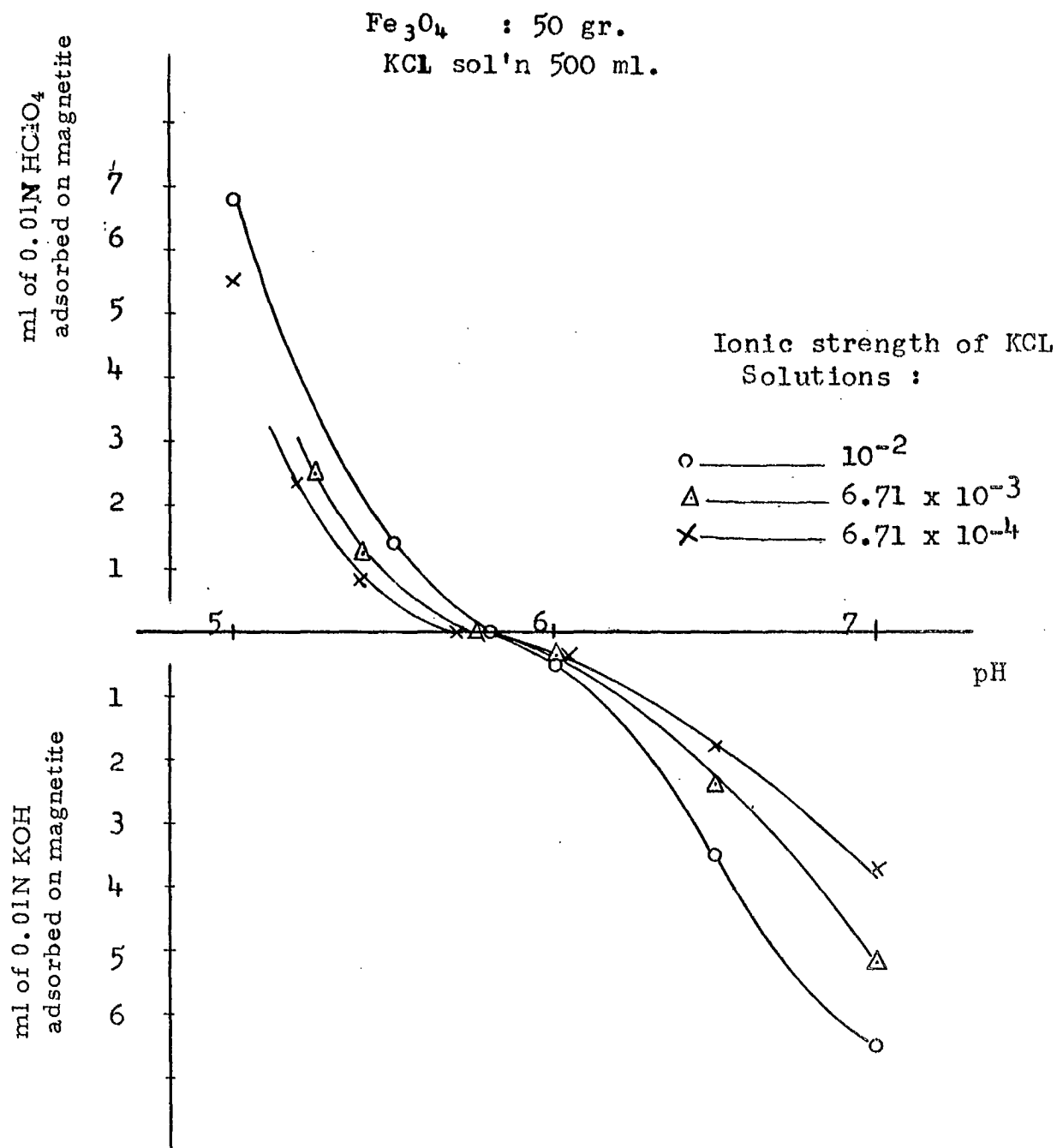Sample Weight : 50 g
Specific Surface : 1970 cm²/g

Figure 5: Potentiometric Titration
of Magnetite

CONCLUSIONS

Studies of surface electrical properties of minerals are very helpful in forecasting their behaviour in aqueous solutions containing flotation reagents.

Values of Z P C obtained from the literature for quartz are pH 2 to 3.7; magnetite, pH 6.5; and chrysotile, pH 11.8. Values obtained by potentiometric titrations were seen to be pH 2.5 for quartz, pH 5.75 for magnetite and pH 10.7 for chrysotile.

Z P C values may be obtained by three methods: potentiometric titrations, electrophoretic mobilities and streaming potential measurements. While the same end result is aimed at, the principles and the characteristics of the three methods differ and the values obtained by these methods can vary. The Z P C values taken from the literature were obtained by streaming potential. A program is now underway to correlate these three methods. It is also most probable that the values of the Z P C depend on the previous history of the mineral, a variable which will be eliminated by suitable procedures.

The potentiometric titration method of obtaining surface charges and Z P C can attain a high degree of accuracy by refinement of techniques and instrumentation. The major drawback is the long period of time required to complete one titration. This problem is now being considered and will be resolved by automating the titration process.

REFERENCES

1. G. A. Parks & P. L. de Bruyn: "The Zero-Point-of-Charge of Oxides". J. Phys. Chem. June 1962, Vol. 66.

2. P. L. de Bruyn & G. E. Agar: "Surface Chemistry of Flotation". 50th Anniversary Volume, AIME, 1962.

3. A. M. Gaudin & D. W. Fuerstenau: "Quartz Flotation with Anionic Collectors". Mining Eng. Jan. 1955.

4. A. S. Joy & D. Watson: "Adsorption of Collector and Potential-Determining - Ions in F lotation of Hematite with Dodecylamine". Bul. IMM No. 685, 1964.