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**(54) Title:** METHOD AND IMMERSION SENSOR TO MEASURE ELECTROCHEMICAL ACTIVITY

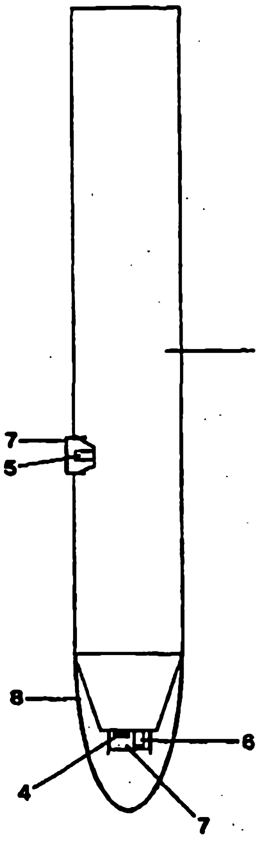
**(54) Bezeichnung:** VERFAHREN UND TAUCHMESSFÜHLER ZUM MESSEN EINER ELEKTROCHEMISCHEN AKTIVITÄT

## (57) Abstract

The invention relates to a method and an immersion sensor to measure electrochemical activity of a layer lying on a molten mass using an electrochemical sensor comprising a measuring cell and a counter electrode. In order to reliably reproduce exact measurements in the layer, the measuring cell and the counter electrode are initially immersed in the molten mass, wherein the measuring cell and the counter electrode are protected before they come into contact with said layer. The measuring cell and the counter electrode are then brought into contact with the molten mass and heated. Subsequently, the measuring cell is pulled up into the layer to carry out measurement, while the counter electrode remains in the molten mass during measurement. To this end, the measuring cell and the counter electrode are provided with a protective cap. The measuring cell is placed above the counter electrode when the sensor is immersed.

## (57) Zusammenfassung

Die Erfindung betrifft ein Verfahren sowie einen Tauchmeßfühler zum Messen einer elektrochemischen Aktivität einer auf einer Schmelze aufliegenden Schicht mittels eines elektrochemischen Sensors, der eine Meßzelle und eine Gegenelektrode aufweist. Um zuverlässig reproduzierbare und genaue Messungen in der Schicht zu ermöglichen, werden Meßzelle und Gegenelektrode zuerst in die Schmelze eingetaucht, wobei Meßzelle und Gegenelektrode vor Berührung mit der Schicht geschützt werden und wobei Meßzelle und Gegenelektrode mit der Schmelze in Berührung gebracht und erwärmt werden. Danach wird die Meßzelle zur Durchführung der Messung in die Schicht emporgezogen, wobei sich die Gegenelektrode während der Messung in der Schmelze befindet. Dazu weisen Meßzelle und Gegenelektrode eine Schutzkappe auf und die Meßzelle ist in Eintauchstellung des Sensors oberhalb der Gegenelektrode angeordnet.



# Method and Immersion Sensor to Measure an Electrochemical Activity

The invention relates to a method of measuring the electrochemical activity of a layer lying on a melt by means of an electrochemical sensor comprising a sensing cell and a counterelectrode.

Furthermore, the invention relates to an immersion sensor for measuring electrochemical activity of a layer lying on a melt, with an electrochemical sensor arranged on a support , the sensor comprising an electrochemical sensing cell and a counterelectrode.

Such a method and such an immersion sensor are known from Radex-Rundschau, No 1, 1990, pp 236-243. There a measuring method of measuring electrochemical activities, specifically the oxygen content of slag layers lying on iron melts was described. Measurement are effected by arranging a conventional electrochemical sensor comprising a sensing cell with zirconium oxide and magnesium oxide as electrolytes and a counterelectrode within the liquid slag layer. The contact of the sensor with the material to be analysed is not accurately defined because of inhomogeneities in the slag so that the readings cannot be reproduced with sufficient accuracy.

A similar sensor has been described in EP 330 264 A1. That sensor is used to determine the level of the melt by determining the phase boundary between the metal melt and a slag layer resting on the metal melt. A method for indirectly measuring electrochemical activities in slag on silver melts has been disclosed in EP 0 450 090 B1. In that method, an electrochemical sensing cell is arranged in a silver melt. The activity in the slag is deduced from the readings.

Starting from the known state of the art, the problem underlying the invention is to provide a method of the generic type with which reliably reproducible and accurate measurements in the layer are possible. Furthermore, the problem of the invention is also to create an immersion sensor suitable for practising the method.

According to the invention, the problem relating to the method is solved in that the sensing cell and the counterelectrode are first immersed in the melt, with the sensing cell and counterelectrode being protected from contact with the layer; that the sensing cell and the counterelectrode are brought into contact with the melt and heated (approximately to the temperature of the melt); that, after that, the sensing cell is withdrawn into the layer for carrying out the measurement; and that the counterelectrode is situated within the melt during the measurement. The measurement is carried out in the usually liquid layer after the sensor temperature has reached the ambient temperature. Equilibration of the temperature is required, inter alia, to prevent solidification of material of the layer at a sensor which is too cold. While the sensor is passed through the layer, the sensing cell and the counterelectrode are protected from contact with the material of the layer by conventional protective caps which dissolve in the melt. Temperature equilibration can be monitored via measurements of the oxygen activity. Once the flat part of the activity on the registered curve has been reached after immersion into the melt, temperature equilibration has been completed. This equilibration can be monitored also with a thermocouple, During the measurements, the counterelectrode is situated inside the melt, ie., in a well-defined environment so that accurate and well reproducible measurement data can be obtained.

The sensing cell and the counterelectrode are conveniently arranged on a support; the counterelectrode is pulled up together with the sensing cell. While the counterelectrode is withdrawn to the (liquid) layer, the electrochemical activity can be measured. In this way, the level of the melt can be determined because a discontinuous change of the electrochemical activity is measured as soon as the counterelectrode reaches the boundary layer between the melt and the (liquid) layer lying on it. Advantageously, during the measurement, the temperature of the melt and/or of the layer is determined. It is also convenient to carry out the measurement during the lifting movement (withdrawal motion) of the sensing cell and counterelectrode. In particular, it is also advantageous to determine the oxygen activity of the melt before the withdrawal of the sensing cell. In this way, the electrochemical activity, particularly the oxygen activity of the melt and of the layer lying on it, can be determined and, in the same measuring cycle, the melt temperature and the bath level of the melt (boundary layer between the melt and the superjacent layer) can be determined with a single sensor so that a separate measurement with an other sensor is unnecessary. Measurements in the melt or in the layer can be carried out also when the lifting motion of the immersion sensor is interrupted; in this case, the sensing cell and the counterelectrode for measuring the oxygen content or some electrochemical activity of the melt are inside the melt, whereas the sensing cell for measuring the oxygen content of the layer is in the same, with the counterelectrode being arranged within the melt. The inventive process can be used to advantage for measurements made in a steel melt and the superjacent layer. The method can be practised also for making measurements in liquid glass and superjacent layers. Therefore, a metal melt or a glass melt of liquid glass are understood as melt within the scope of the invention. The determination of the oxygen activity in a slag layer lying on a steel melt makes it possible to draw conclusions on the content of slag components other than iron oxide. This has been described in detail, for example, in the above-listed state of the art.

According to the invention, the problem for an immersion sensor is solved in that the sensing cell and the counterelectrode have a protective cap and that, in the immersed position of the sensor, the sensing cell is arranged above the counterelectrode. In this way, a fixed spacing of the sensing cell from the counterelectrode is obtained and the sensing cell and the counterelectrode are moved simultaneously, with the spacing between them being maintained all the time.

It is convenient to configure the support means as a support tube and to arrange the sensing cell at, or in, the side wall of the support tube, and the counterelectrode, on the front face of the support tube. It is also advantageous to arrange the sensing cell in an opening in the side wall of the support tube. In an other advantageous embodiment, both the sensing cell and the counterelectrode are arranged at the immersed end of the support tube, and the counterelectrode is mounted at a holder attached to the immersed end of the support tube so that its active part has the required spacing from the sensing cell. Furthermore, for obtaining optimal measurement data, it is advantageous to arrange the longitudinal axis of the sensing cell perpendicular to the longitudinal axis of the support tube. As is well known and described in detail in the literature, such sensing cells are usually configured as tubes which are closed at one end and made from a solid electrolyte material having the reference electrode inserted in it in a reference material.

It is further convenient that the spacing of the sensing cell from the counterelectrode (in the longitudinal direction) is at least 2cm because this spacing accounts with the greatest possible safety for a tolerance region resulting from the transition region between the melt and the superjacent layer. It is ensured in this way that the counterelectrode indeed can be arranged in the melt during measurements in the layer. Furthermore, it is convenient to arrange a thermocouple at the immersed end of the support means in order to determine the melt temperature in a simple way.

An embodiment of the invention is explained below in greater detail with reference to a drawing. In the drawing, there show:

Figure 1, an immersion sensor with a sensing cell arranged at the side;

Figure 2, an immersion sensor with a sensing cell arranged at the front face;

Figure 3, a schematic representation of the measuring method through various positions of the immersion sensor; and

Figure 4, the electrochemical voltage in the course of the measurements.

The immersion sensor illustrated in Figure 1 comprises a support tube 1 at which an electrochemical sensor is arranged for measurements in a slag layer 2 above a steel melt 3. Signal lines are run to data processing instruments from the electrochemical sensor through the support tube 1 and a conventional spear rod attached to support tube 1 for its use. The electrochemical sensor, which comprises a sensing cell 5 and a counterelectrode 4, is initially protected by conventional protective caps 7 on the counterelectrode 4 and the sensing cell 5. The protective caps 7 can be made, for example, from cardboard or metal or a combination of the two materials. The immersed end of the support tube 1 is additionally protected by a metal cap 8. The counterelectrode 4 is arranged at the immersed end of the support tube 1 of the sensor, whereas the sensing cell 5 is arranged (in the direction of immersion) a few centimetres above the counterelectrode 4. A thermocouple 6 is mounted near the counterelectrode 4. The counterelectrode 4 can be ring-shaped. The thermocouple 6 can be arranged within this ring-shaped counterelectrode 4 and, accordingly, can be mechanically protected by the counterelectrode 4. The thermocouple 6 measures the temperature in close vicinity of the counterelectrode 4.

Figure 2 shows an other possibility of configuring the electrochemical sensor in which the sensing cell 5 and the counterelectrode 4 are mounted at the immersed end of the support tube 1. The sensing cell 5 is enclosed by a protective cap 7 within which a thermocouple 6 is mounted and which provides mechanical protection. The counterelectrode 4 has a spacing of 40 cm from the sensing cell 5 and is arranged at the end of a holder 9 attached to the immersed end. In this way the counterelectrode 4 situated at the tip has a sufficient spacing from the sensing cell 5. The holder 9 can have the form of a tube through which the connecting lines of the counterelectrode are run in insulated fashion. The counterelectrode 4 and the sensing cell 5 are protected by a common protective cap 8.

It is also possible to arrange the counterelectrode 4 not at the support tube 1 but at the crucible accommodating the steel melt 3, eg., on the bottom of the crucible. In this case, a protective cap is not required because the counterelectrode 4 is not in contact with the slag layer 2 (however, the bath level can not be determined with this arrangement).

For making a measurement, the electrochemical sensor is first immersed through the slag layer 2 into the steel melt 3 so that both the counterelectrode 4 and the sensing cell 5 are situated within the steel melt 3. When passing through the slag layer 2, the sensor is protected by the protective caps 7, 8 from contact with the slag and adhesion of the same. This state is characterised in Figure 3 as position A. The sensor is heated in the steel melt 3, whereby temperature equilibration with the steel melt 3 is achieved. During this process, the protective caps 7, 8 are dissolved (position B). In position C illustrated in Figure 3, first the oxygen activity (the oxygen content) of the steel melt 3 is measured. After that, the electrochemical sensor is withdrawn upwards until the sensing cell 5 is above the steel melt 3 in the slag layer 2. There the oxygen activity in the slag layer 2 is measured either during the upward motion or while the sensor is at rest (position D).

After that, the sensor is pulled further upwards, out of the steel melt 3. As soon as the counterelectrode 4 leaves the steel melt 3, ie., enters into the boundary layer 10 between the steel melt 3 and the slag layer 2, the voltage measured with this method increases suddenly so that the boundary layer 10 between the steel melt 3 and the slag layer 2, ie., the level of the metal (steel melt 3),is clearly indicated (position E).

The spacing of the counterelectrode 4 from the sensing cell *5* is chosen greater than the thickness of the boundary layer 10 between the slag layer 2 and the steel melt 3; a spacing of about 2 cm will suffice in some instances. A spacing of about 40cm proved to be practicable.

In this way, the oxygen content of the steel melt 3, the oxygen content of the slag layer 2, and the bath level (boundary layer 10) can be determined in succession.

Figure 4 shows the change of the voltage during the measurement. The height h of the sensor is plotted to the abscissa, and the measured electrochemical voltage U is indicated on the ordinate. The partial oxygen pressure can be calculated from the voltage in the generally known fashion. The various positions are denoted by the same letters as the positions shown in Figure 3. Position A indicates the voltage when the sensing cell 5 and the counterelectrode 4 have been immersed in the steel melt, ie., at the beginning of the measurement, before temperature equilibration. In position C, the sensing cell 5 is inside the steel melt 3 the oxygen activity of which is measured. In position D, the sensing cell 5 is in the slag layer 2, whereas the counterelectrode 4 is situated in the steel melt 3 so that the activity in the slag layer 2 is being measured. Position E shows the sudden increase in voltage when the counterelectrode 4 exits from the steel melt 3.

## The claims defining the invention are as follows:

1. A method of measuring an electrochemical activity of a layer lying on a melt by means of an electrochemical sensor comprising a sensing cell and a counterelectrode, characterised in that the sensing cell and the counterelectrode are first immersed in the melt, with the sensing cell and counterelectrode being protected from contact with the layer; that the sensing cell and the counterelectrode are brought into contact with the melt and heated; that, after that, the sensing cell is withdrawn into the layer for carrying out the measurement; and that the counterelectrode is situated within the melt during the measurement.

2. The method according to claim 1, characterised in that the measurement is carried out in a steel melt and in a superjacent slag layer.

3. The method according to claim 1 or claim 2, characterised in that the sensing cell and the counterelectrode are arranged at a support and that the sensing cell is lifted together with the counterelectrode.

4. The method according to any one of claims 1 to 3, characterised in that the oxygen activity of the melt is determined before the sensing cell is withdrawn out of the melt.

5. The method according to any one of claims 1 to 3, characterised in that the measurement is made while the withdrawal motion of the sensing cell and the counterelectrode takes place.

6. The method according to any one of claims 1 to 5, characterised in that the temperature of the steel melt and/or of the slag layer is determined during the measurement.

7. A method of measuring an electrochemical activity of a layer lying on a melt by means of an electrochemical sensor substantially as hereinbefore described with reference to the accompanying drawings.

8. Immersion sensor for measuring an electrochemical activity of a layer lying on a melt, with an electrochemical sensor arranged at a support and comprising an electrochemical sensing cell and a counterelectrode, characterised in that the sensing cell and the counterelectrode have a protective cap and that, in the immersed position of the sensor, the sensing cell is situated above the counterelectrode.

9. The immersion sensor according to claim 8, characterised in that the support is configured as a support tube and that the sensing cell is arranged at, or in, the side wall of the support tube and the counterelectrode, at the immersed end of the support tube.

10. The immersion sensor according to claim 9, characterised in that the sensing cell is arranged in an opening in the side wall of the support tube

11. The immersion sensor according to claim 8, characterised in that the support is configured as a support tube and that the sensing cell is arranged at the

immersed end of the support tube, with the counterelectrode arranged at a holder attached to the immersed end of the support tube.

12. The immersion sensor according to any one of claims 8 to 11, characterised in that the spacing of the sensing cell from the counterelectrode is at least 2cm.

13. The immersion sensor according to any one of claims 8 to 12, characterised in that a thermocouple is arranged at the immersed end of the support.

14. Immersion sensor for measuring an electrochemical activity of a layer lying on a melt, substantially as hereinbefore described with reference to the accompanying drawings.

**Dated 2 September 1998**

**HERAEUS ELECTRO-NITE INTERNATIONAL N. V.**

**Patent Attorneys for the Applicant/Nominated Person**

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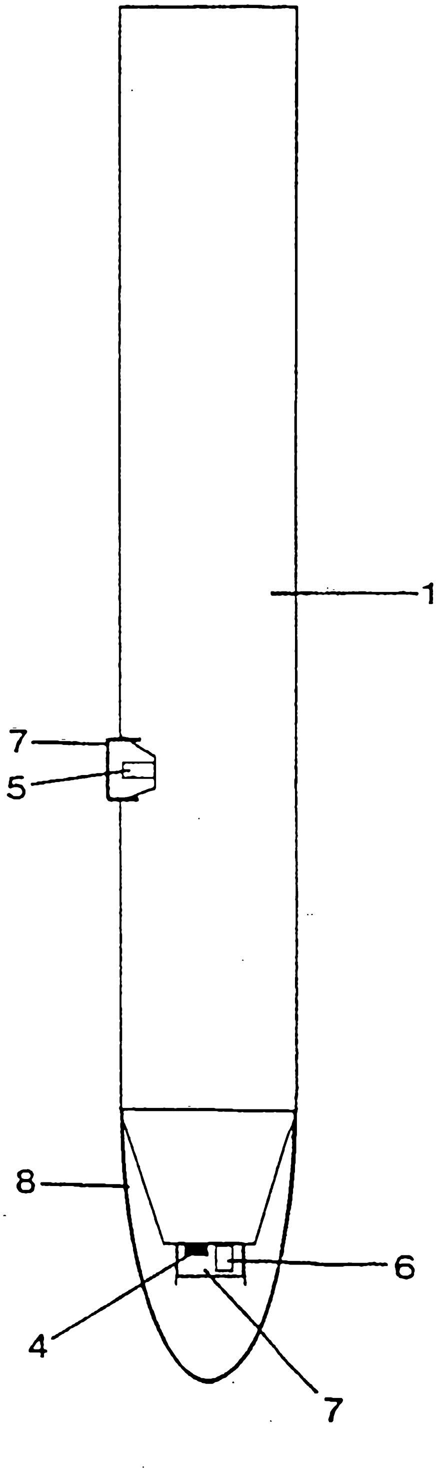

Fig.1

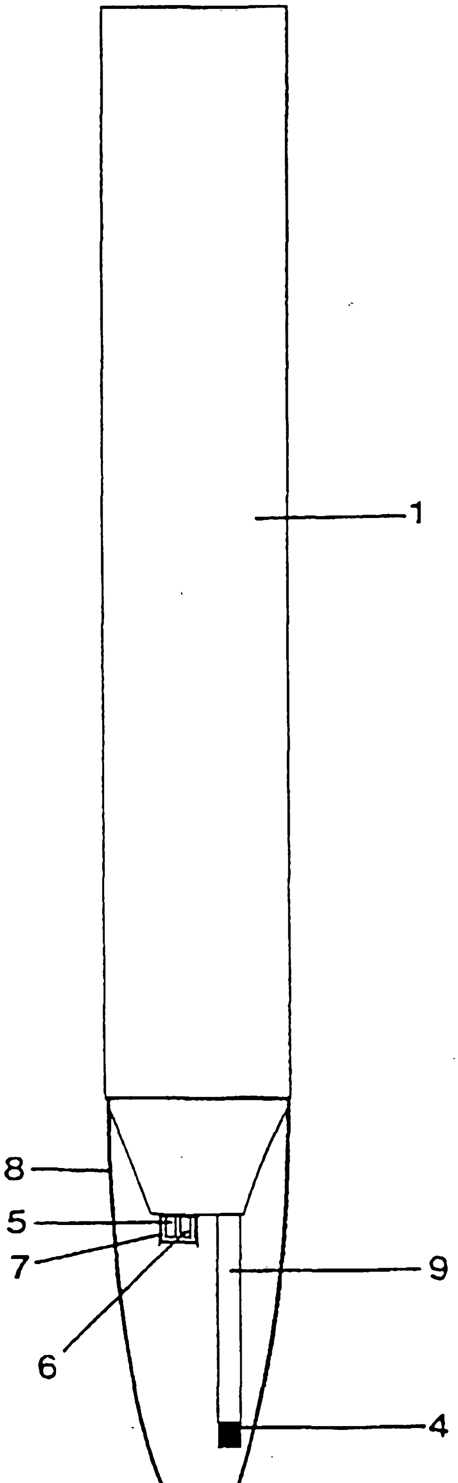

Fig. 2

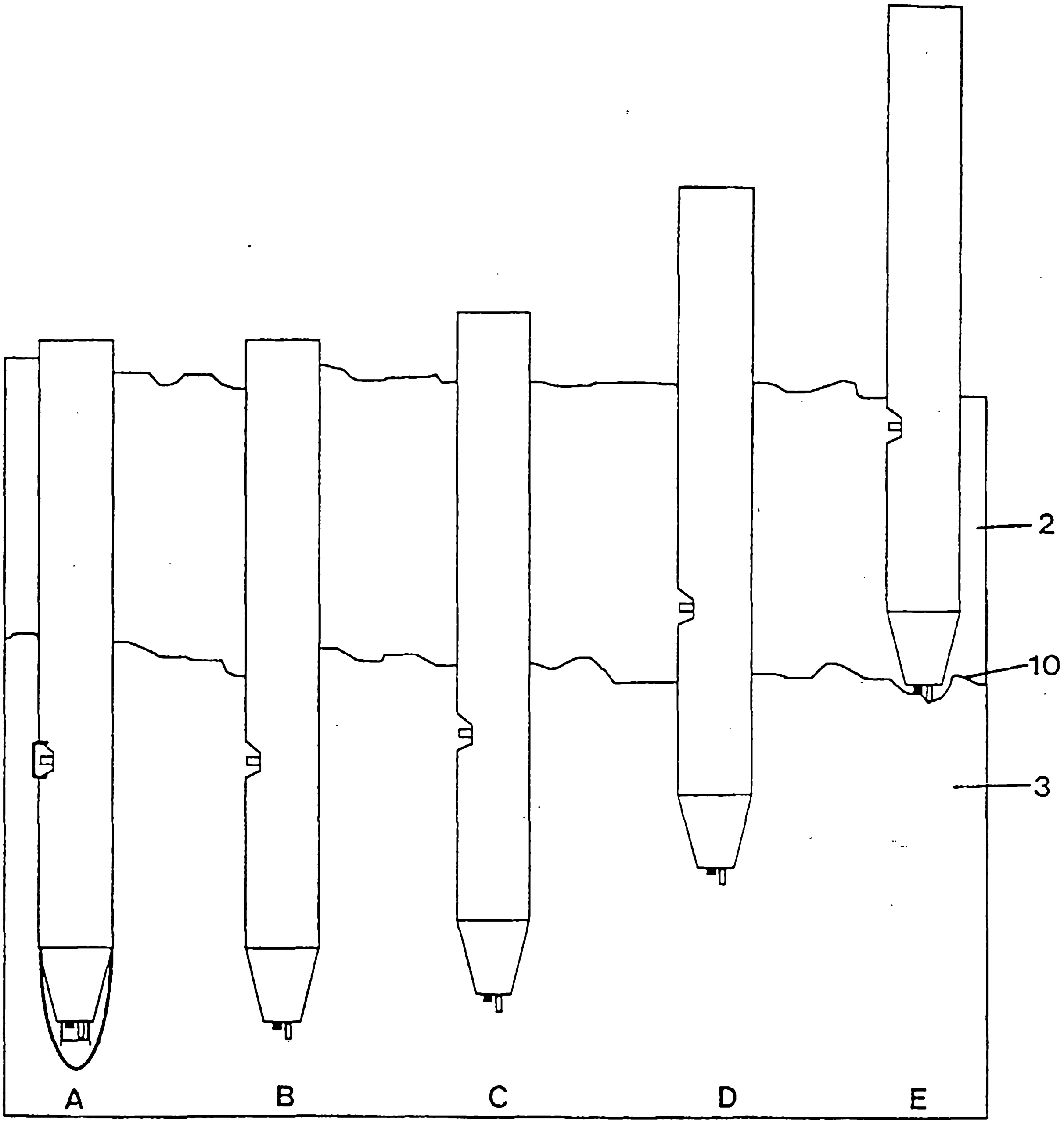

Fig.3

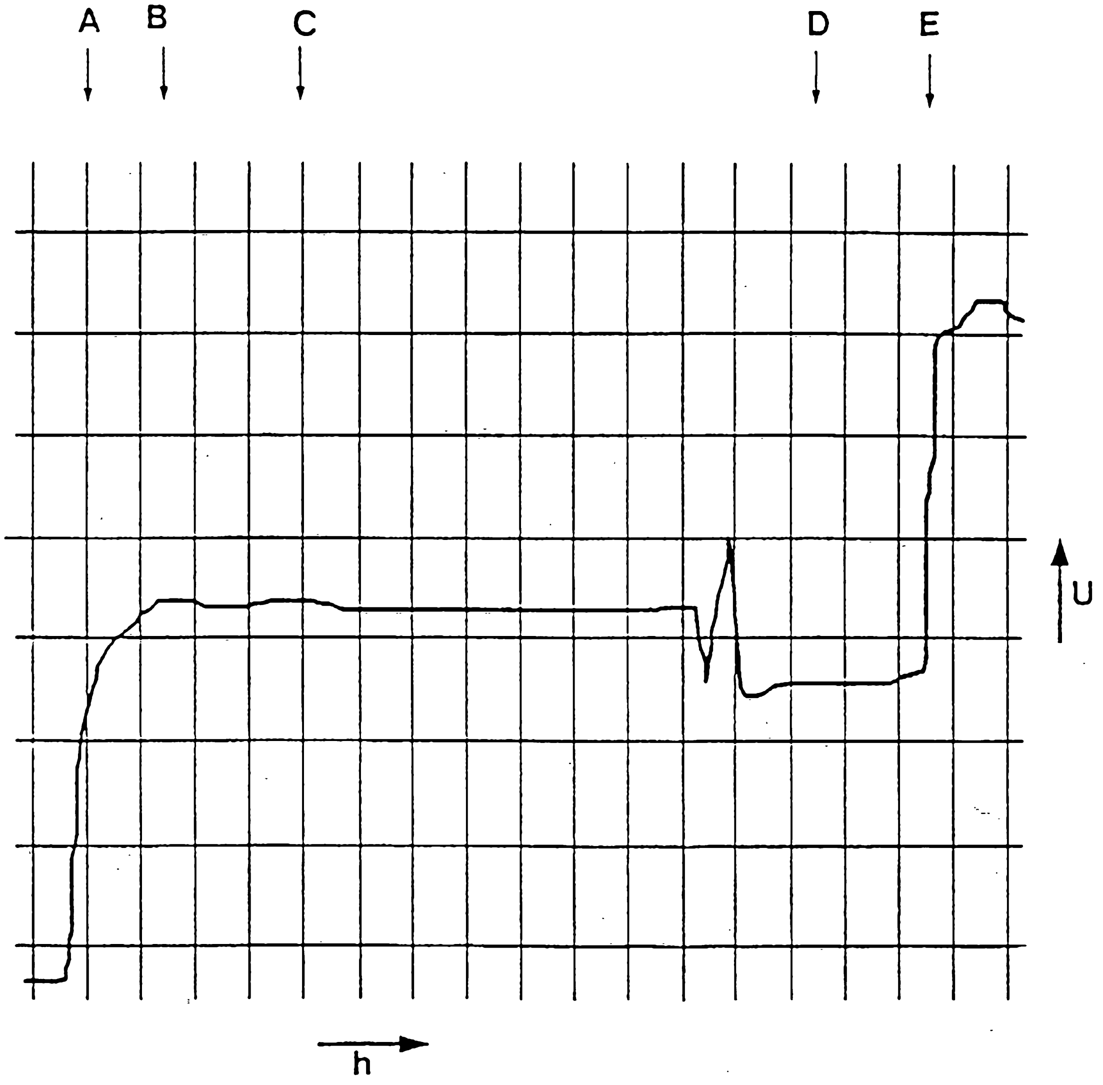

Fig.4