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CARRIED OUT DURING COMPLEX TESTS
OF THE A-1 REACTOR**



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ABSTRACT

Remote corrosion measurements in the A-1 reactor serve to the frequent supervision of corrosion situation in heavy water circuit and to the control of inhibitor dosage.

Corrosion environment consists of heavy water, saturated with carbon dioxide at temperature of 90° C and pressure of 65 at. It circulates in primary circuit at a velocity up to 3 m/sec, water temperature varies from 40° to 90° C.

As a basis for this measurement and control, corrosion probes, placed in piping of heavy-water circuit out of the reactor, are used. Each probe is used for two types of measurements: instantaneous corrosion rate and instantaneous corrosion attack behaviour.

For measurement of the instantaneous corrosion rate method of polarization resistance, according to Stern and Geary, is used. Determination of corrosion attack behaviour is carried out on the basis of current transients observed in macroelement, which consists of two electrodes, both made from the same metal of interest.

Corrosion problems connected with the use of Al-Mg-Si type of aluminium alloy for the active core callandria, some piping and mechanisms that are working in the A-1 reactor under heavy-water environment (pH = 3.5 and high conductivity as a result of dissolved carbon dioxide under high pressure) have enforced the use of inhibitor and the creation of device system for tracing of corrosion situation during reactor operation.

Electrochemical methods, described below, serve as a part of this above mentioned system.

These methods are used for current supervision of the inhibition effect and by this way undirectly to the supervision of effective inhibitor concentration. This is very significant for operational control of periodical inhibitor dosage into circuit. Moreover they currently give information on the corrosion attack character in measuring point and by this way they undirectly serve as treshold indicators of dangerous component concentrations in water.

Described electrochemical measuring methods have been able to realize in the A-1 reactor only in very simplified form; that's why all measured values must be criticized very carefully and every possible opportunity might be used for their comparison with real corrosion situation.

Measuring equipment, realized in the A-1 reactor, enables to trace the instantaneous corrosion attack character and to measure the instantaneous uniform corrosion rate in Al-Mg-Si type of aluminium alloy in heavy-water circuit. For both types of measurements the same probes are used.

Corrosion attack character is traced according to the Czechoslovak patent, based on the principle of characteristic

current transitions in macroelement created by two electrodes both made from the same material of interest. In the case of uniform attack the current of this macroelement is constant in time; in the case of pitting attack, which is accompanied by gas bubbles formation in pits, characteristic time changes of current take place.

Instantaneous uniform corrosion rate is measured by the method of polarization resistance, proposed by Stern and Geary. This method has been elaborated in detail for our purpose to present reproducible values in wide interval of corrosion rates.

Scheme of probes locations in heavy-water circuit is given in Fig. 1.

One temporary probe was built-in into hot-collector during so-called reactor complex tests, which were carried out in non-active conditions and with light-water environment. Purpose of these tests lies in the confirmation of the serviceability of individual devices before physical start-up. This probe worked under pressure of 65 at and temperature up to 90° C, but it was not designed for radioactive operation. Original probes, which moreover must suit requirements on radiation stability of sealing and insulating materials, were prepared in that time; they will be built-in before physical start-up. Original probe No. 1 will be built-in into cold-collector and original probe No. 2 into hot-collector.

Temporary probe which successfully worked for 3,600 hours during reactor complex tests is seen in Fig. 2.

This probe consists of a container, in which polyamide filler is closely deposited. In this filler two pairs

of cylindrical electrodes made from material of interest (Al-Mg-Si type of aluminium alloy) are again closely deposited. One pair is determined for regular measurement, the second one for some supplementary experiments. Functional surfaces of electrodes are placed on faces in the plane of inner surface of tubing. By this way it is secured that electrodes do not interfere the flow character in measuring point. Fig. 3 shows the functional surfaces before the probe was built-in. Original probes for radioactive operation will consist only from two electrodes.

In the place under the probe cover these electrodes are connected with Pyrotenax cable using hermetic ceramic terminal of Ferranti; Pyrotenax jacket is soldered into the cover. In this place transducer for water leakage is also placed-in. This transducer would indicate the case of the tightening of electrodes in filler and/or entering of water to contacts between electrodes and Pyrotenax cables.

Corrosion probe is built-in into piping according to Fig. 4.

Translational speed of the water flow in measuring point reaches 3.3 m/sec, which corresponds to the maximum velocity of water flow in flow-off tubing in reactor active core area.

Corrosion probes are connected with the help of 60 m long cable to the measuring equipment in block supervision room - see Fig. 5. Main parts of this measuring equipment, that are operated from the front panel face, include recorder of EZ 4 type, switch box and mirror galvanometer. Circuit diagram can be seen in Fig. 6. Switches are used, on the one hand, for connecting of transducers No. 1 or No. 2, and on the other hand for choosing of measurement type - either for tracing of corrosion attack character, or for measurement of the instantaneous corrosion rate. - see Fig. 7

During tracing of corrosion attack character the current transitions between two electrodes in the same probe are registered; both electrodes are connected in outer circuit through small resistance. To explain the significance of such a measurement we show results of one laboratory test. During this test pitting corrosion was artificially caused in the same material using the anodic polarization; simultaneously the potential of studied electrodes with respect to the reference saturated calomel electrode was measured, current transitions between two studied electrodes were registered and corroded surfaces were microscopically observed. Scheme of this laboratory circuit diagram is shown in Fig. 8. Results received during this experiment enabled to interpret the reasons of current instability in macroelement, formed by two electrodes from the same material, during pitting type attack.

Fig. 9 contains records of current transition in macroelement at different potentials with respect to the reference electrode. Above certain value of potential, characteristic periodical changes began to appear; their frequency grew according to the showed curve. At simultaneous microscopic observation it was found out that pitting corrosion took part in single small pit which gas bubbles were released from. Frequency of bubbles creation and release precisely agreed with record.

During another experiment similar measurements were carried out, but with the help of microscopic examination it was determined that pitting attack took part in several small pits. Interference of these several working pits was the reason for disturbing of record periodicity, as it is shown in Fig. 10.

On the basis of these experiments we impute the current instability of macroelement at pitting attack to the bubbles of gas released in corrosion pit; at the same time interference of more working points usually takes place, but periodical time behaviour also can appear in case of one working point.

For completeness it is necessary to add that during these experiments it has not been determined the existence of so-called critical potential, that would reach some reproducible values for given material and corrosion environment. On the contrary it was found out that first indications of bubble release from corrosion points appear at different potentials depending on operations made with this electrode formerly.

For corrosion probe used in reactor complex tests there exists the record of pitting attack and of uniform attack - see Fig. 11. This probe was tested in experimental loop of the VUCHZ Brno at parameters analogous to the A-1 case with the difference that in circuit only tap water circulated. In this environment pitting attack occurred; it was characterized by record which sample is placed in right-hand part of this figure. In one part of these tests even periodical effects appeared for short time, their oscillographic record is shown in Fig. 12.

After the completion of tests in experimental loop the probe's face was mechanically machined and then whole probe was built-in into heavy-water circuit of the A-1 reactor; during complex tests it was used at different intervals for attack character tracing. In all cases only time behaviour according to uniform attack, was measured: see left-hand part of Fig. 11. During visual inspection of this

probe after complex tests it was confirmed that no pitting took part.

A great number of papers, dealing with question of uniform corrosion rate measurements by means of polarization resistance is collected up to this date, so we are pointing out only some characteristic peculiarities connected with its use in the A-1 reactor.

For this type of measurement only one aluminium electrode in probe is connected, it functions as an indicative electrode. As a reference and at the same time as a polarizing electrode serves the piping chassis.

Measurements are realized by use of separate measuring actions, which consist of switching on the chosen constant polarizing current from hard power supply between indicative electrode and chassis for time interval unavoidably necessary for the determination of proper overvoltage value to calculate the inverse value of polarizing resistance. Records of measuring actions at different corrosion rates are illustrated in Figs. 13 and 14.

Successful application of polarization resistance measurements depends on the determination of proper overvoltage values. This problem is very wide and that's why we point out only some practical conclusions:

- a) Measuring action must not last for unnecessarily long time, to avoid serious damaging of original surface condition.
- b) Between two measuring actions there is necessary to ensure sufficient recovery period.
- c) In records, given in Figs. 13 and 14, overvoltage value at higher corrosion rates corresponds to the fast chan-

ge just after switching on the polarizing current and the measuring action lasts for only several seconds. At lower corrosion rates, caused either by the effect of environment parameters or by the effect of inhibitor, the overvoltage value corresponds to the steady-state value and the measuring action lasts for tens of seconds or longer.

- d) Polarizing current density must be chosen by such a way to range in the area of initial linear part of polarization curve. In all cases that may occur at the A-1 reactor parameters, current densities, causing overvoltage values up to 20 mV, can be used with safety.

Polarizing current density divided by overvoltage value is equal to the inverse value of polarization resistance; using the calibration graph which has been determined previously, it is possible to find the instantaneous uniform corrosion rate in units of mm/year. This calibration graph has been determined by special calibration experiments carried out in simple laboratory conditions and in test pressure-water reactor loop. The results of electrochemical measurements were compared with the results of conventional weight evaluation - see Fig. 15.

During complex tests of the A-1 reactor it appeared to be very useful to record the potential of aluminium electrode against chassis not only at polarization measurements but also during longer time intervals. Chassis has relatively constant potential even at different parameters of corrosion environment while potential of aluminium electrode depends on these parameters essentially. All it is clearly seen in Fig. 16, which represents the records obtained during the initial working period of the circuit.

At low corrosion rates of aluminium alloy of interest its potential reached values around 300 mV (chassis +, aluminium alloy -). Good agreement has been received between the low corrosion rate in this range of potentials and the overvoltage transients behaviour during the measuring action, used for the determination of polarization resistance. Increase in corrosion rate was accompanied by the shift of the aluminium electrode potential towards the less noble values (up to 900 mV). At the same time changed the overvoltage transient behaviour during the measuring action.

In later stages of complex tests similar effects were observed if dosing the inhibitor. At high corrosion rate the potential reached values around 1,000 mV and after the addition of inhibitor, when corrosion rate was lowered practically to zero, the potential shifted to values around 200 mV.

Moreover it was found out that the potential sensitively follows even those changes in corrosion environment parameters, which do not affect the instantaneous corrosion rate; hereby we can obtain different supplementary informations.

Complex reactor tests, including operation pauses, when exchange of water in heavy-water circuit was realized, lasted almost for 5,000 hours, but only for about 3,900 hours the circuit was full of water. For the main part of this time - i. e. for 3,600 hours - corrosion measurement was carried out. Only for interval of about 300 hours measurement was interrupted because of failure in sealing between corrosion cover and nozzle flange in piping. This was

the only one more serious defect that occurred at operational application of above described corrosion methods; moreover it was caused by temporary building-in. This defect cannot repeat during regular operation as the probe's cover will be welded to the nozzle flange.

Simplified course of the instantaneous corrosion rate during complex tests is given in Fig. 17. Time intervals of run I + run IV and operational interruptions are also marked in this diagram.

At first stages of the complex tests the corrosion environment parameters in heavy-water circuit (temperature, CO₂, flow) were very unsteady and changed in a wide range. The instantaneous corrosion rate followed very strongly these parameter changes and varied in the range of 0.001 + 0.68 mm/year. Only in the course of run IV the steady parameters were reached in the circuit - it enabled to carry out experimental inhibitor dosage and measurements of its effect on the instantaneous corrosion rate.

Some cases, selected from initial stage of complex tests illustrate the influence of the heavy-water pump stoppage and repeated starting - Fig. 18.

It is obvious that the instantaneous corrosion rate was influenced first of all by pump starting, accompanied by abrupt increase (almost of 35° C) in water temperature at measuring point. Rapid changes of proper translational flow velocity did not cause immediate changes of the instantaneous corrosion rate. This conclusion follows from the course character in the neighbourhood of pump stoppage.

One of the most important experiments, carried out with the equipment for remote corrosion measurements, dealt with the experimental dosage of inhibitor H₃PO₄ into the

circuit. The record of this experiment is shown in Fig. 19.

Rapid decrease of the initial corrosion rate value (0.35 mm/year), occurred several minutes after the beginning of desing operation, i. e. immediately at the moment, when water with inhibitor reached the measuring point. At the same moment the shift of potential to the noble region took place. During following hours this decrease slowly continued to unmeasurable values below 0.001 mm/year. In this way the inhibition effect continued for the whole rest of the experiment, i. e. approximately for 2,000 hours, with exception of short-time transition interval when functional surfaces of electrodes became cracked as a result of polyamide filler dilatation (as it was later observed during visual checking of the probe). By this way part of the fresh surface was denuded but it was again passivated, that's why the probe was again finding out practically zero corrosion rate.

At the end it is possible to conclude that during complex tests of the A-1 reactor the appropriation of described electrochemical measurement for tracing of corrosion situation in heavy-water circuit was demonstrated. After building-in of original probes and after examination in active conditions during energetic reactor starting-up, the described methods will become as a part of regular reactor operational control.

left piping area
of callandria vessel

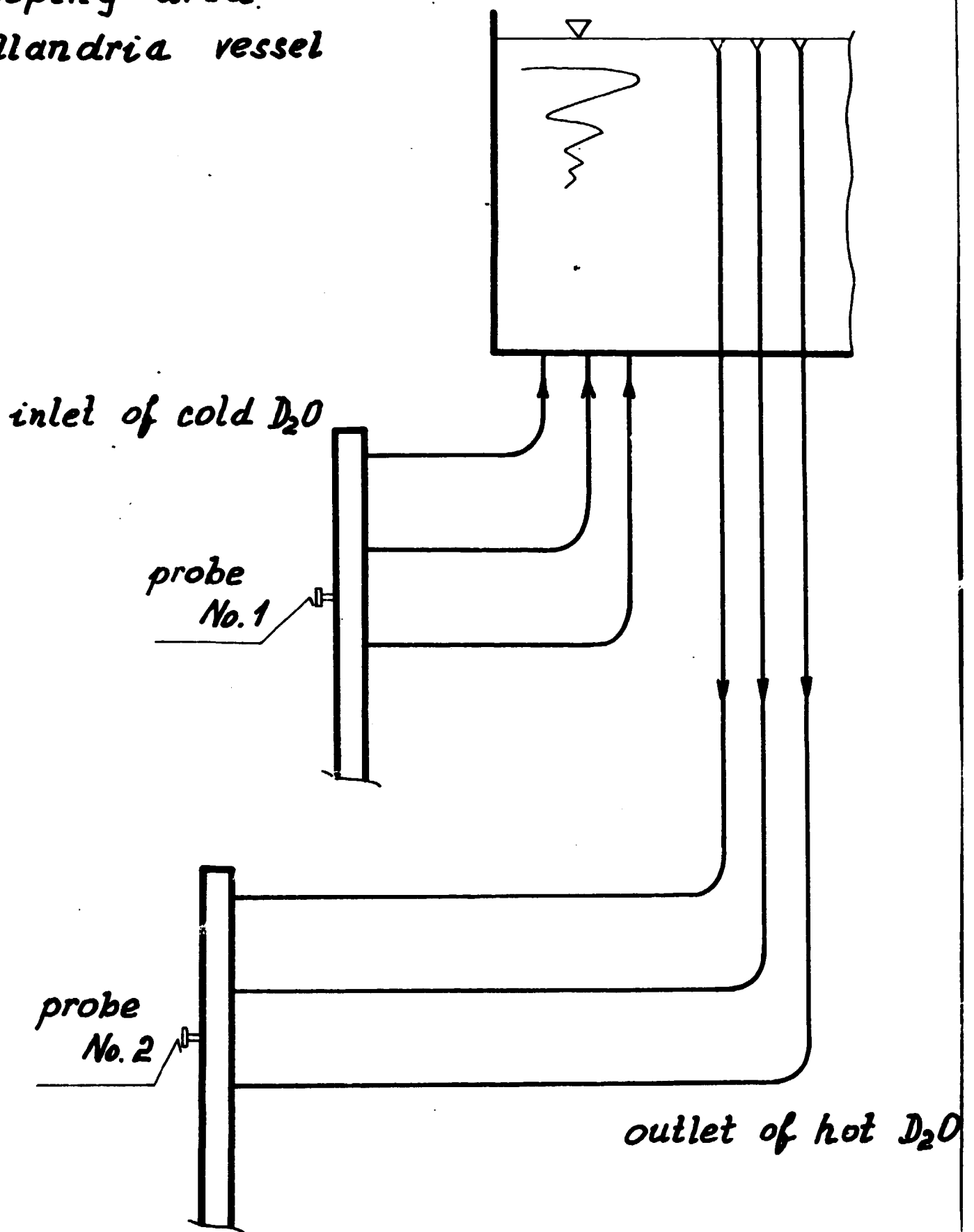


Fig. 1 : Location diagram of corrosion probes
in circuit

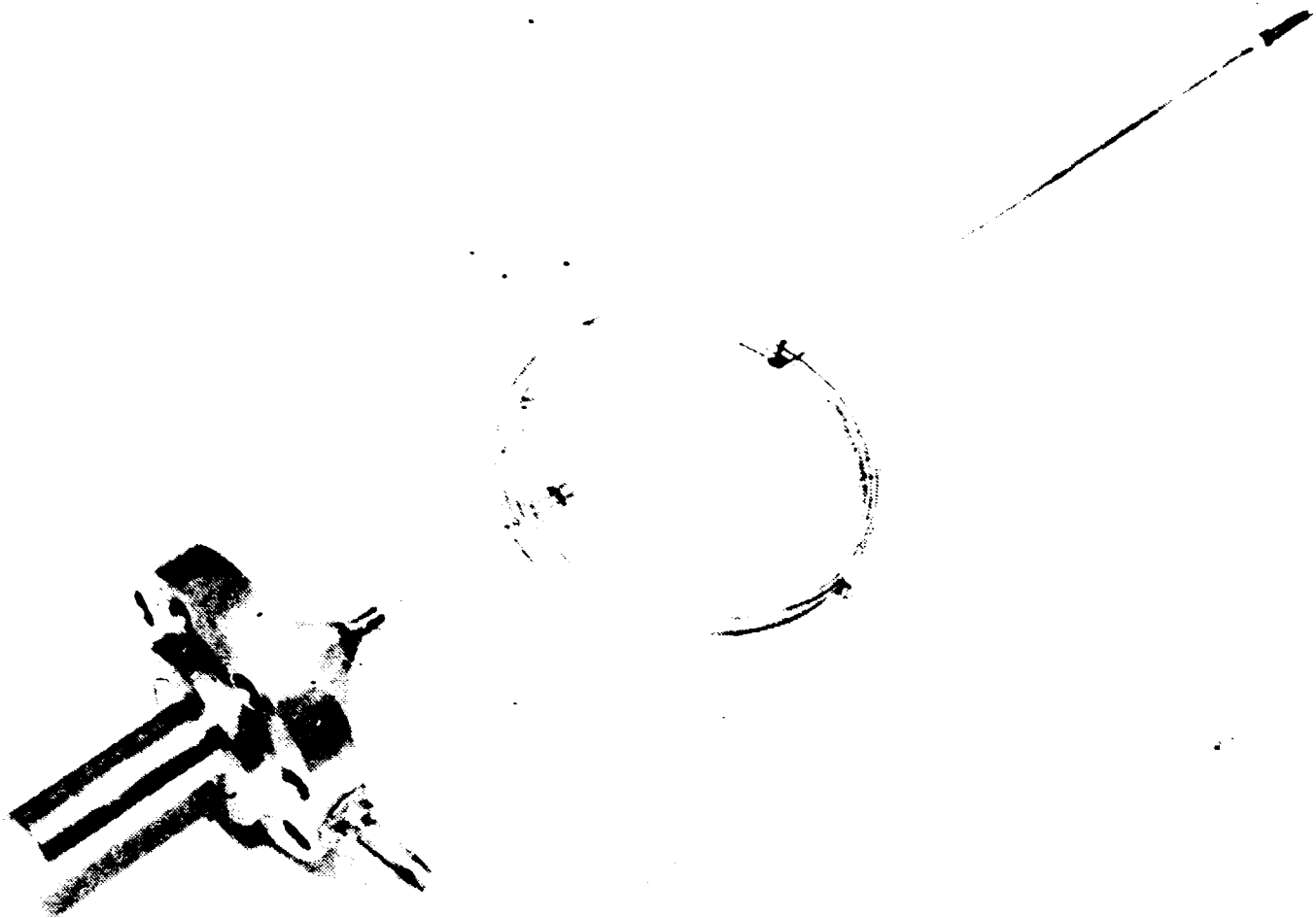


Fig. 2 : Corrosion probe

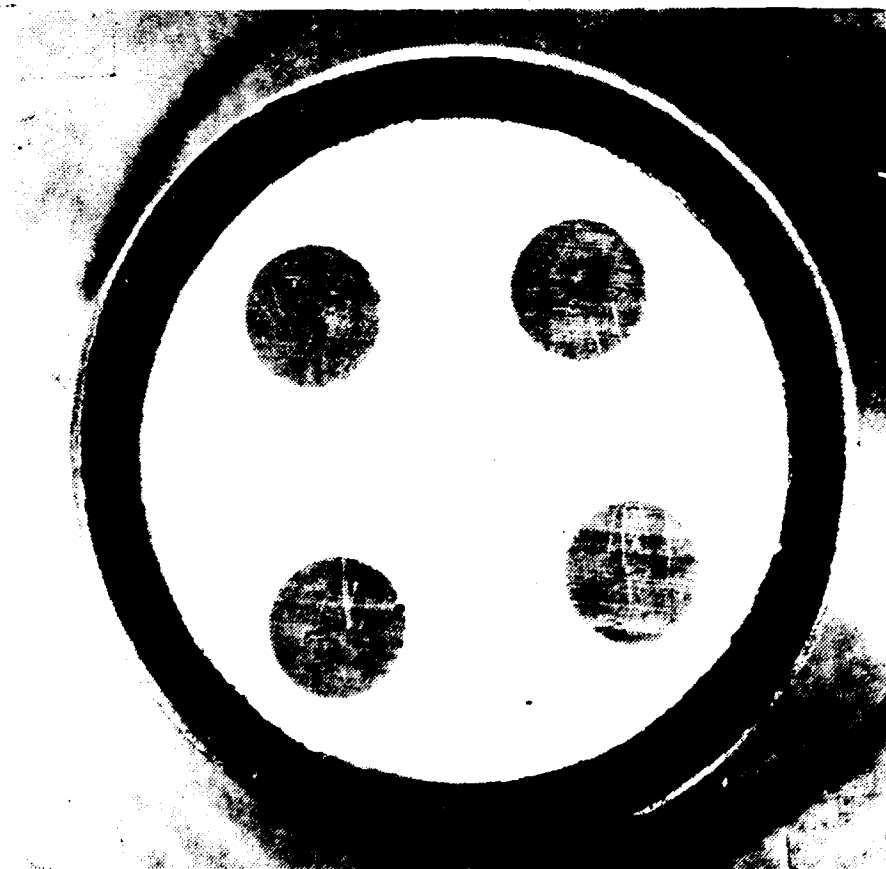


Fig. 3 : Probe's face - functional surfaces of electrodes



Fig. 4 : Corrosion probe installed in heavy water collector

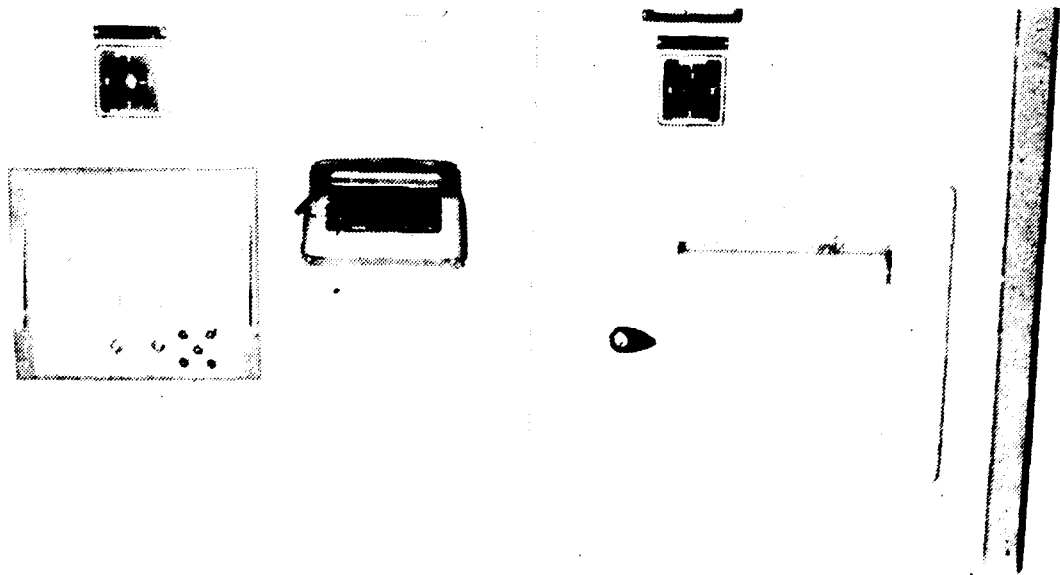
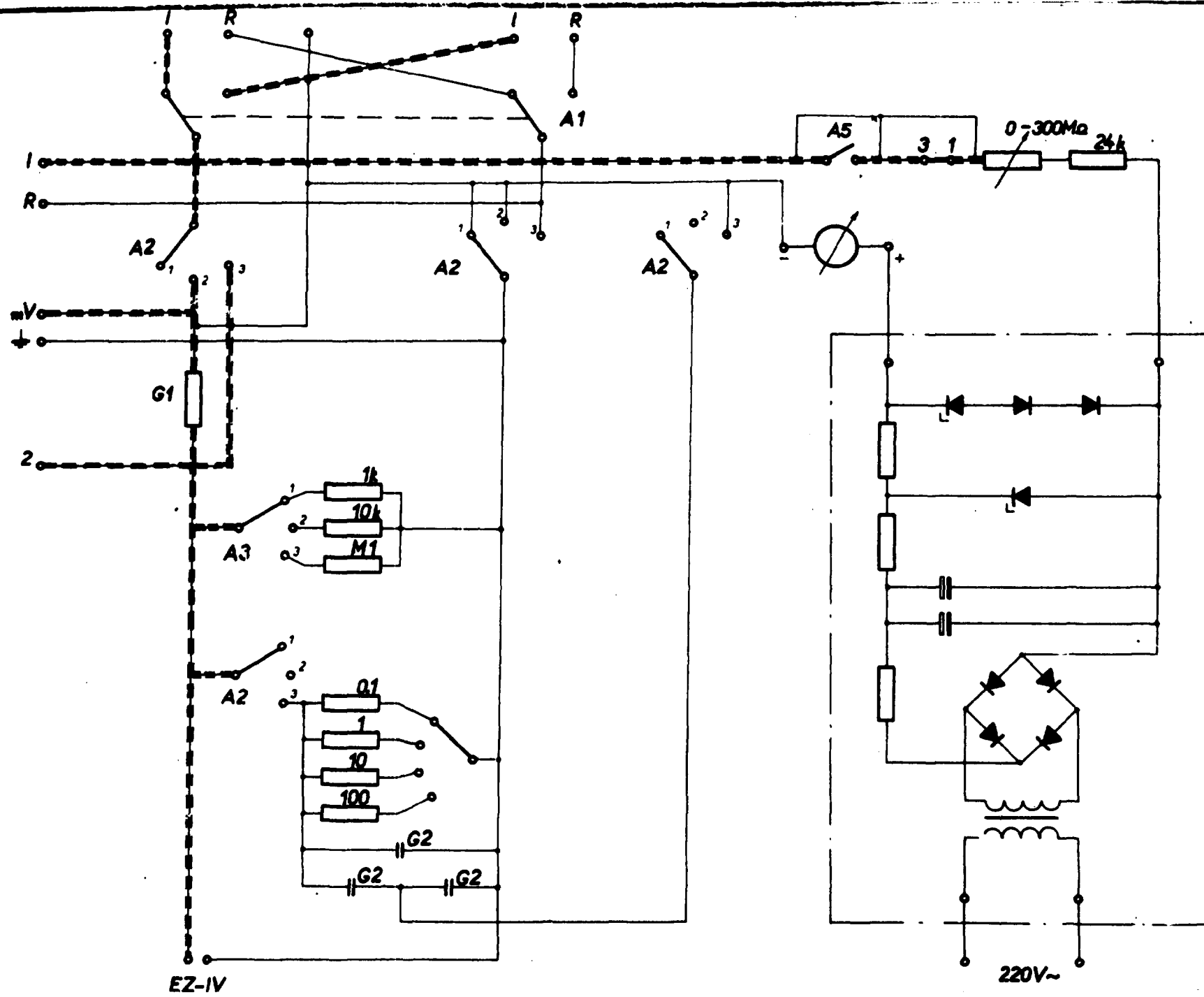


Fig. 5 : Measuring equipment



Switch A2 positions :

- 1 - electrode checking
- 2 - measurement of polarisation resistance
- 3 - pitting tracing

Fig. 6 : Circuit diagram of the measuring equipment for corrosion tracing

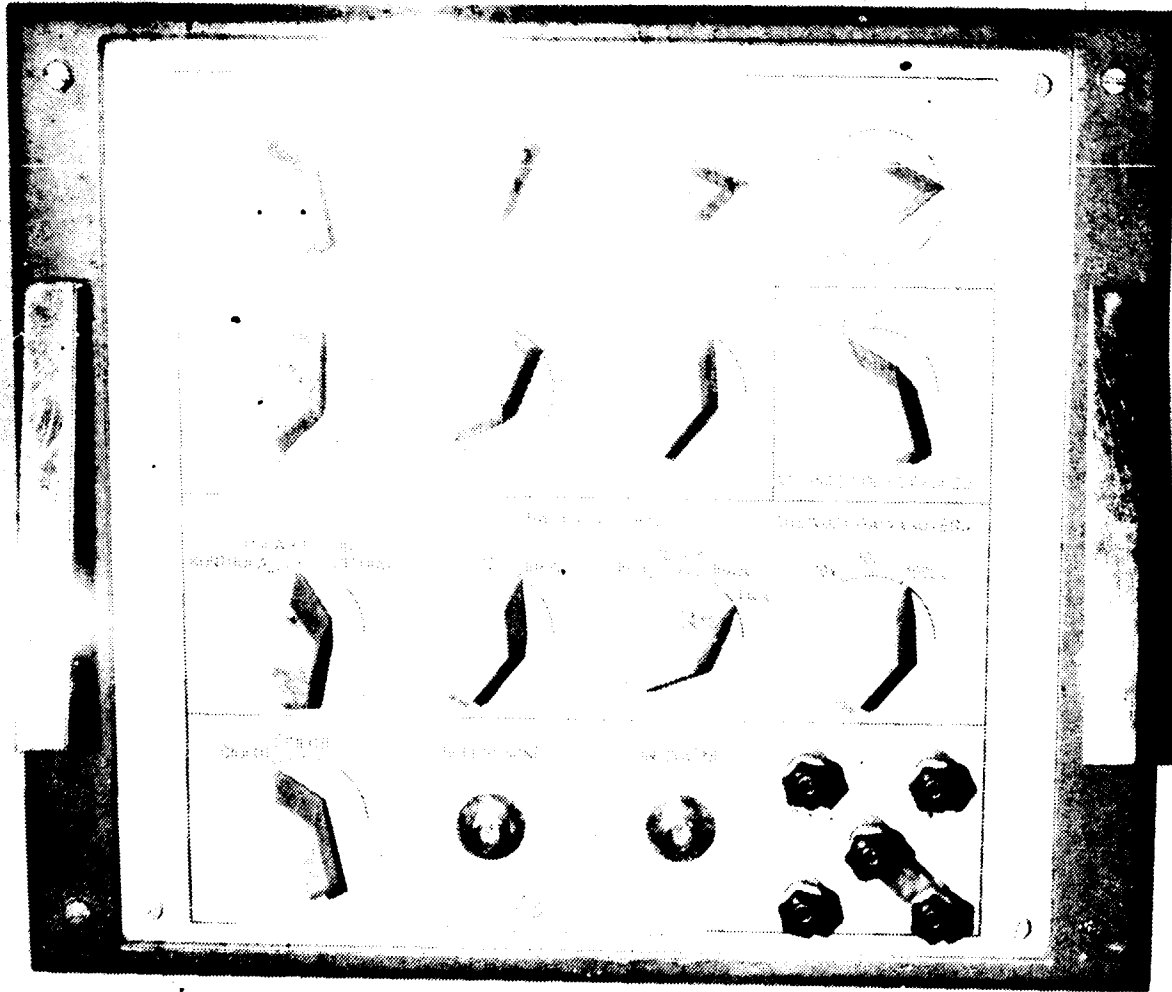
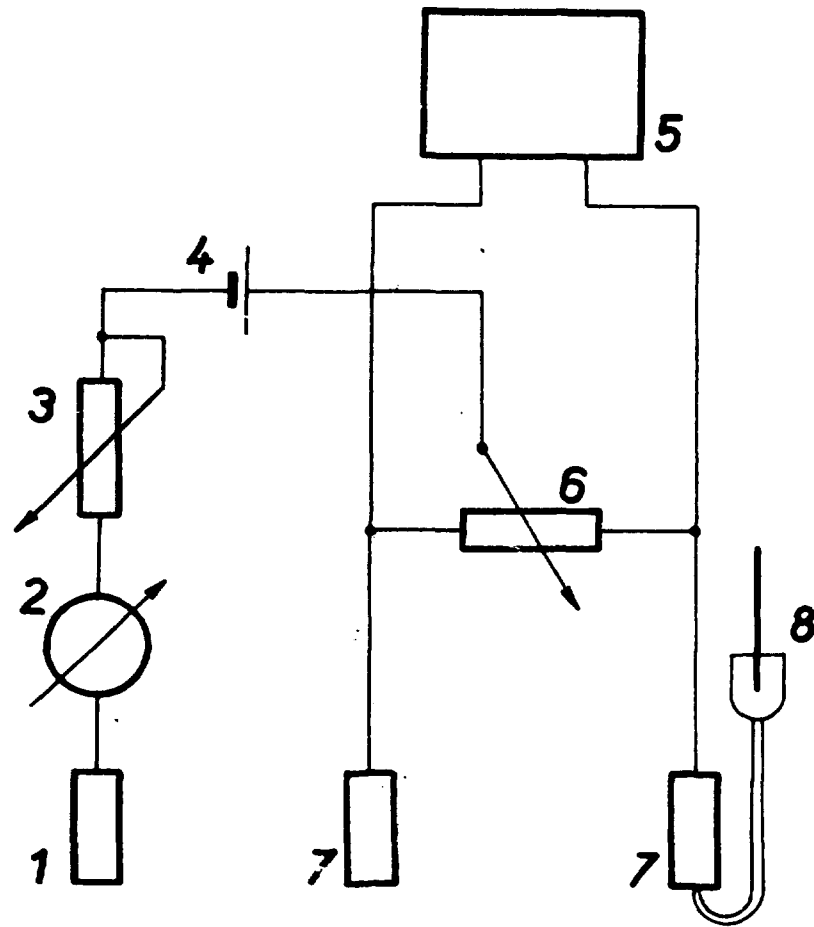


Fig. 7 : Switch box



- 1 - polarization electrode
- 2 - microammeter
- 3 - resist. decade up to 100M Ω
- 4 - d.c. supply
- 5 - record. mV-meter
- 6 - resist. decade up to 10 Ω
- 7 - test electrodes
- 8 - calomel electrode

Fig. 8 : Circuit diagram for tracing of pitting at anodic polarization

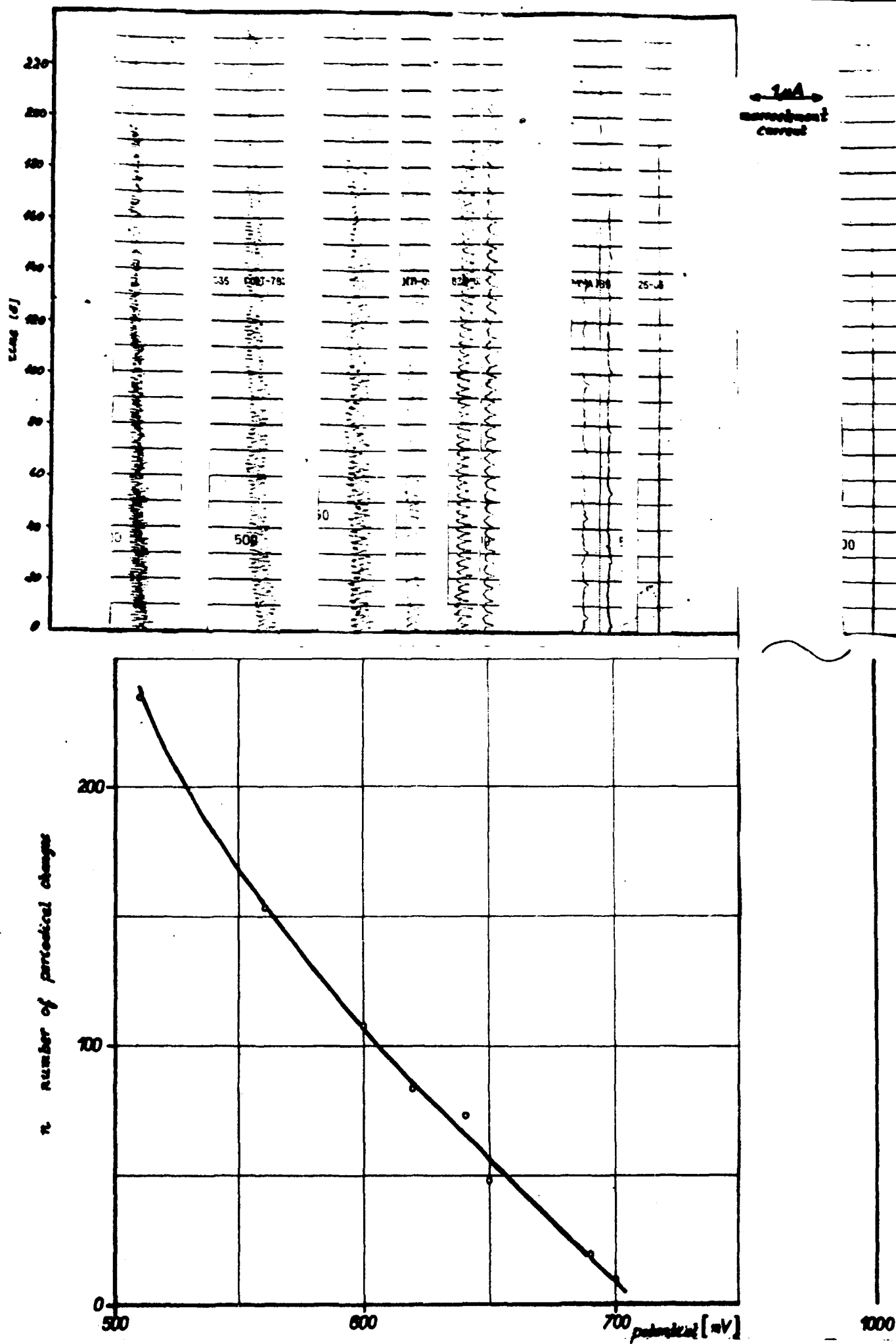


Fig. 9 : Pitting corrosion - characteristic records, corresponding to one working corrosion point, at which bubbles are periodically released / anodic polarization, dil. KCl, 24°C, potential measured against sat. calomel electrode /.

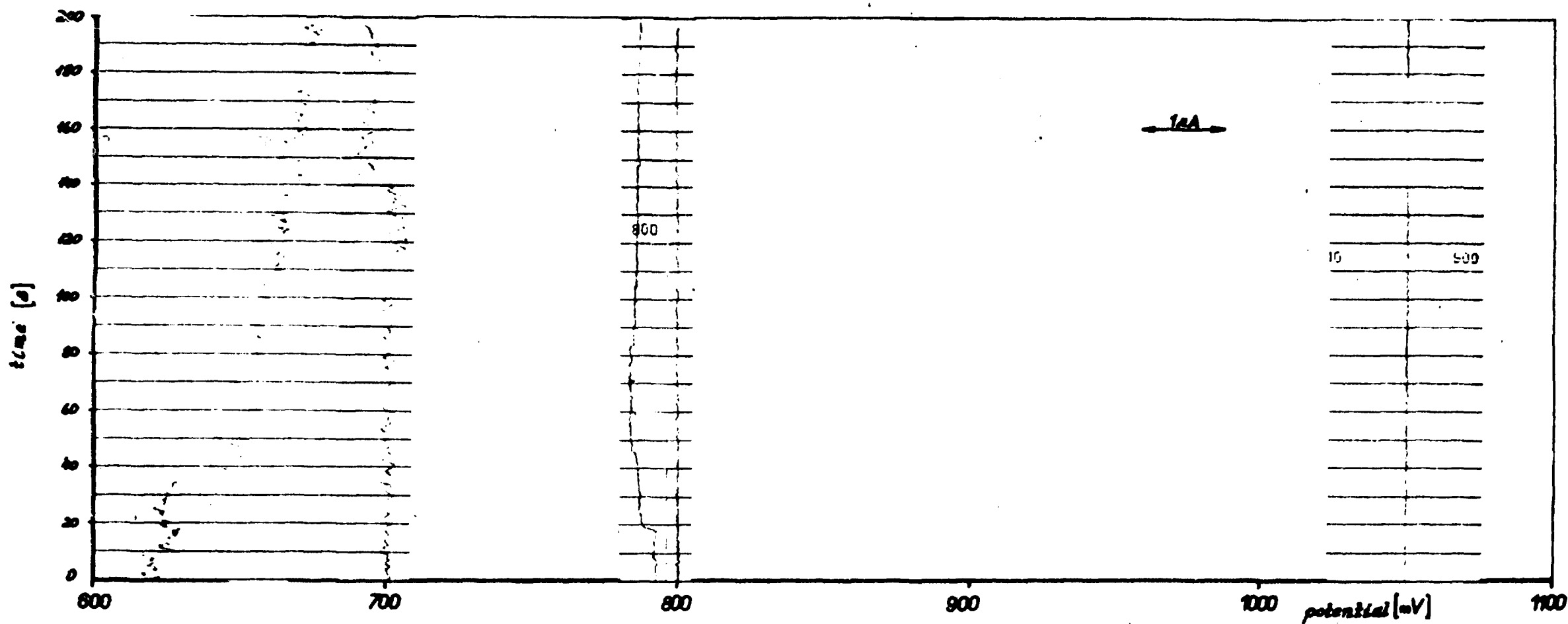
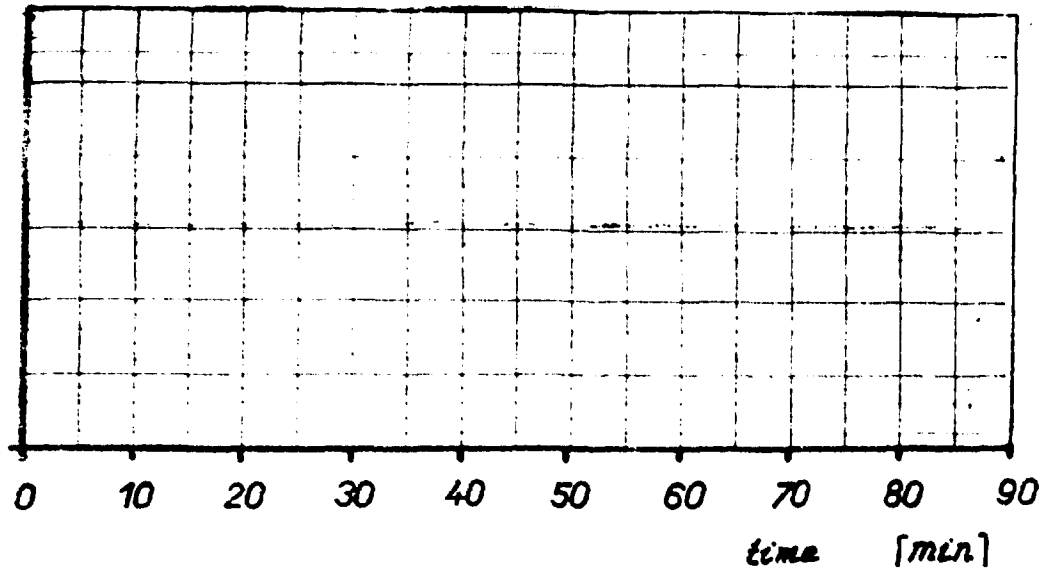


Fig. 10 : Pitting corrosion - characteristic records corresponding to the interference of more working corrosion points / the same conditions as Fig. 9 /

uniform attack - heavy water circuit of reactor A1



pitting attack - tap water in experimental loop

macrocell current
1 μ A

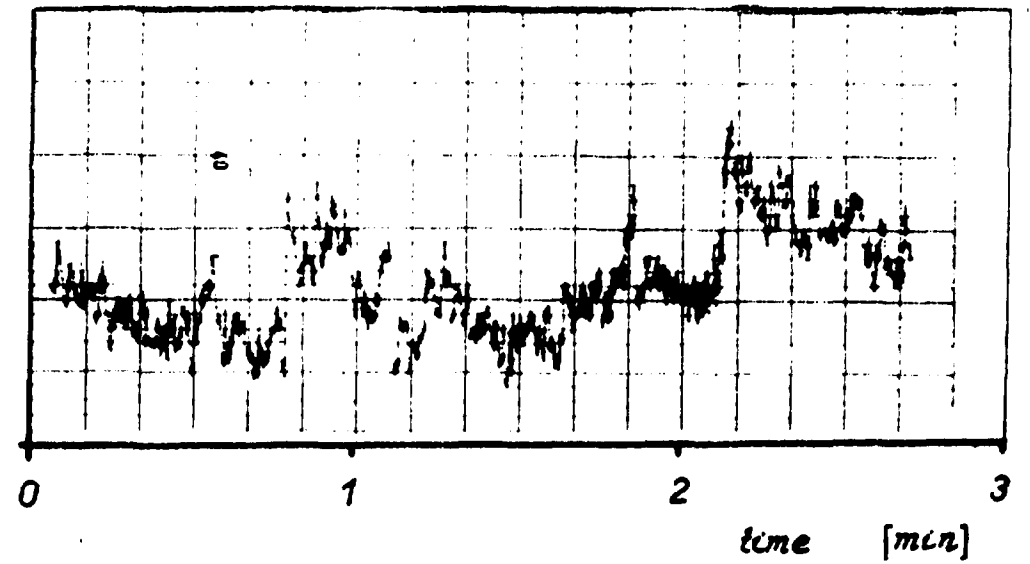


Fig. 11 : Records of uniform and pitting corrosion attack

Fig. 12 : Oscillograph record of pitting in one working corrosion point

Measured in Al reactor, $P_{H_2} = 14 \text{at}$, $t_{\text{water}} = 80^\circ\text{C}$
both curves - water without inhibitor, but different corrosion rates due
to the unsteady conditions in the circuit

curve ① - polarizing current $1 \mu\text{A}$
curve ② - polarizing current $92 \mu\text{A}$

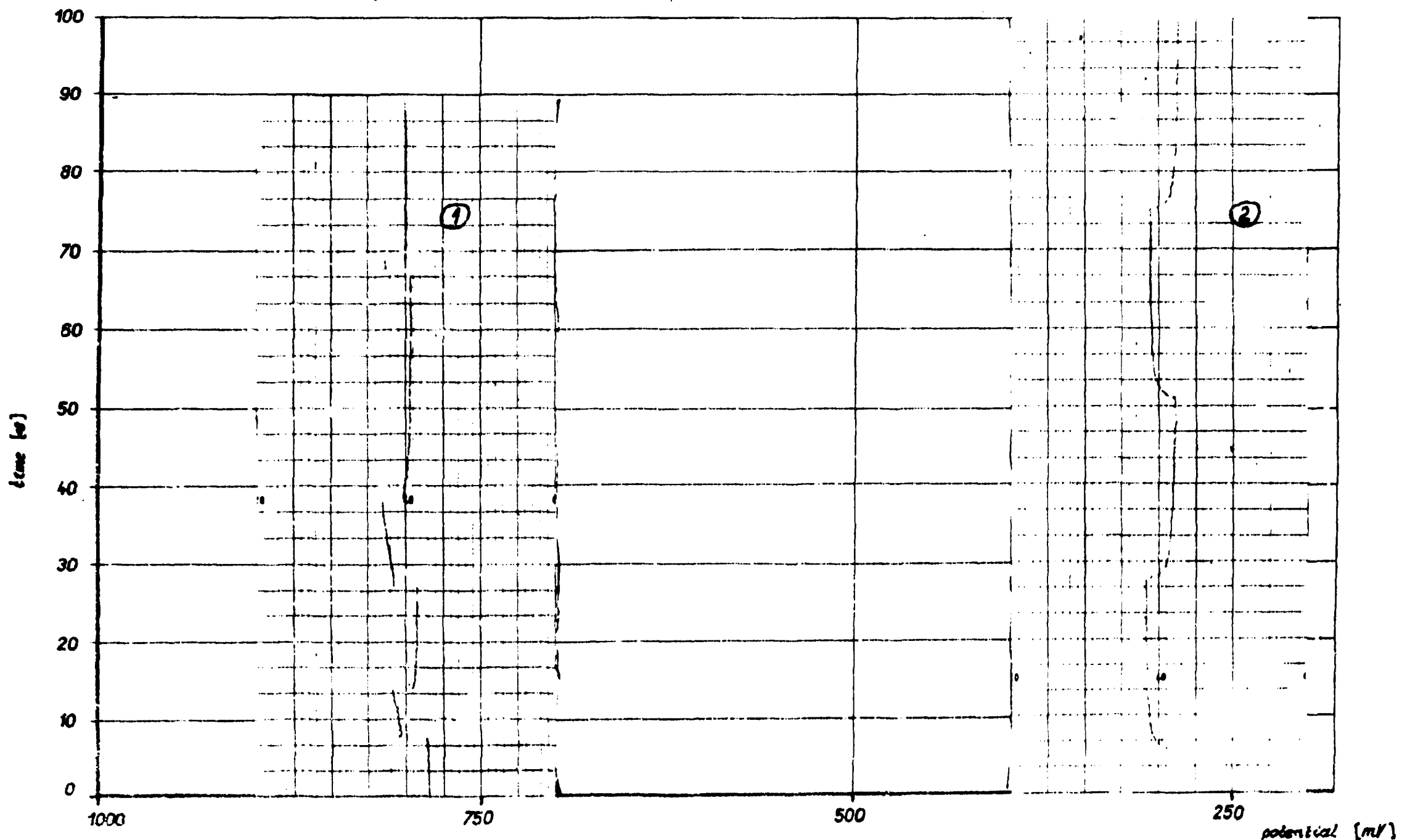


Fig. 13 : Records of overvoltage transients for const. polarizing current

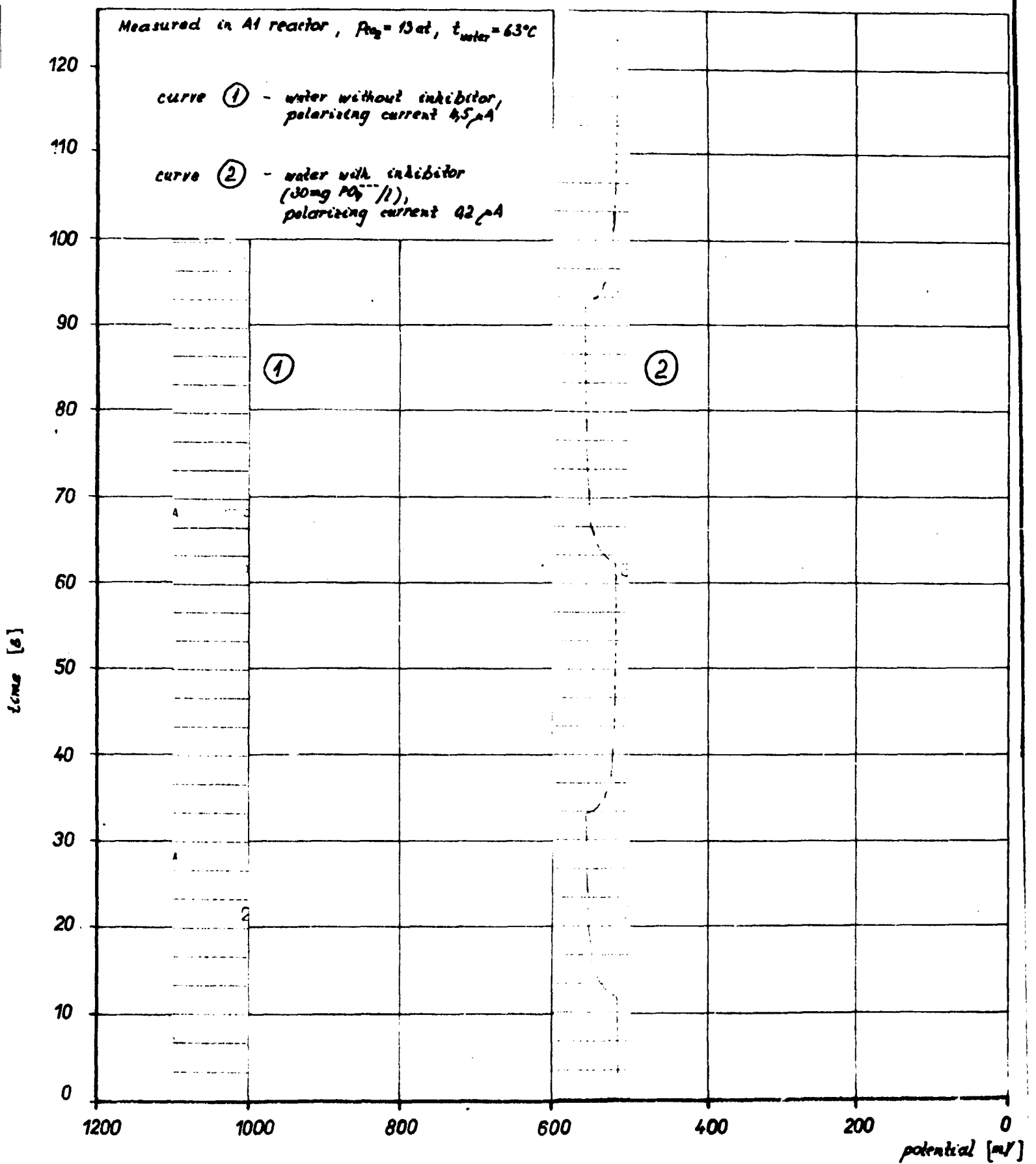


Fig. 14 : Records of overvoltage transients for const. polarizing current / supplement to Fig. 13 /

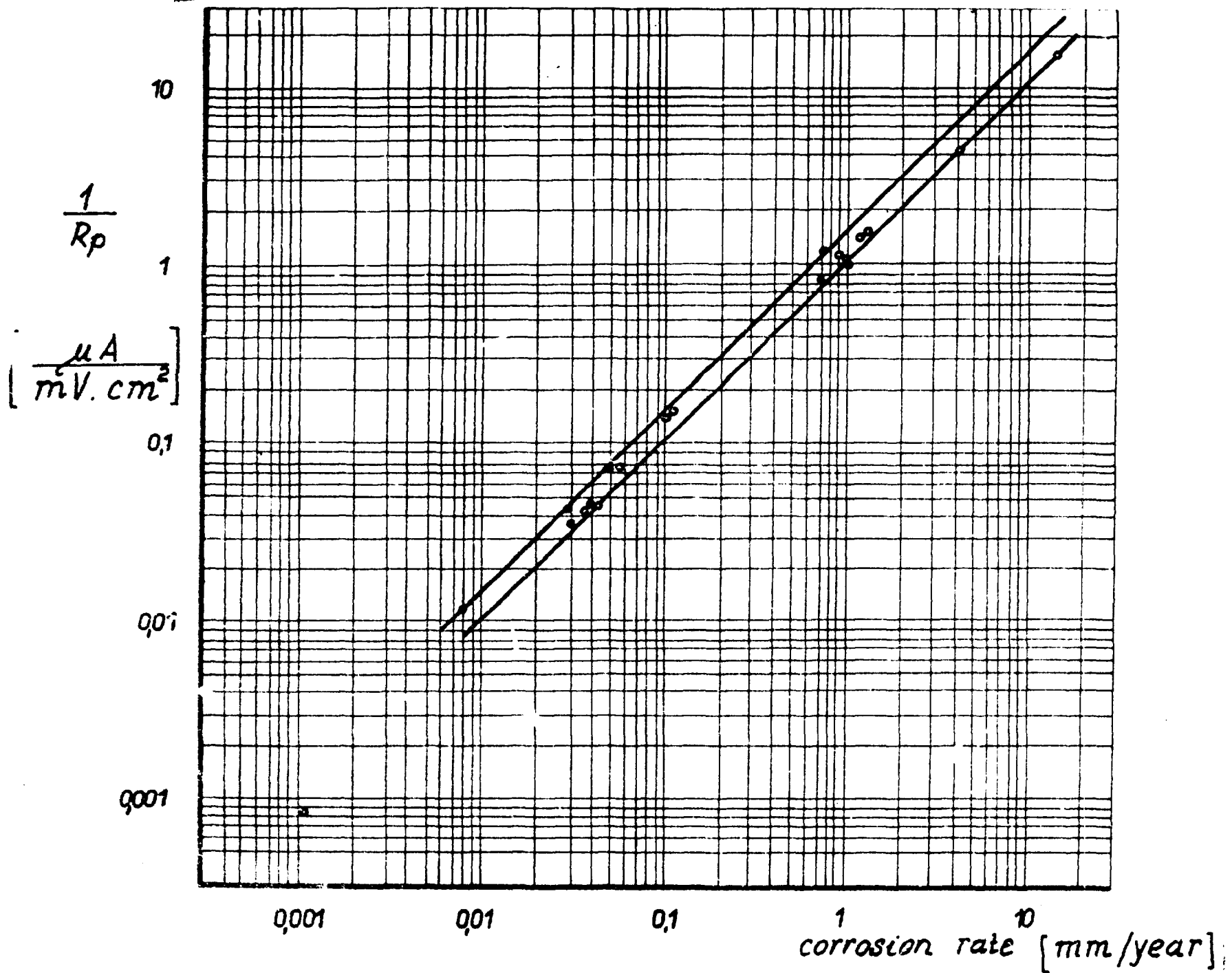


Fig. 15 : Calibration graph of $\frac{1}{R_p}$ vs corrosion rate. Material Al-Mg-Si, 40°C.

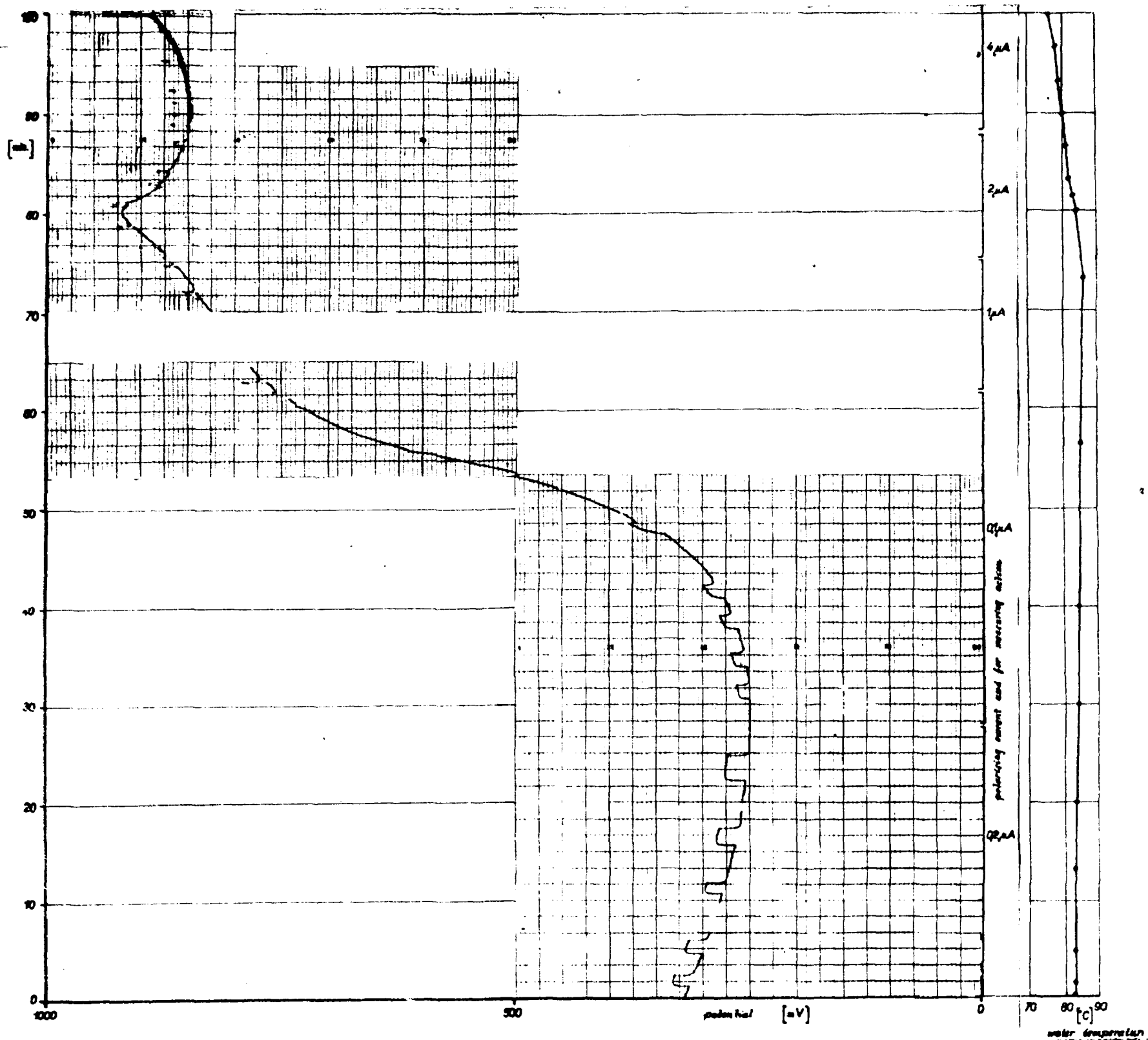


Fig. 16 :
 Changes in potential
 and corr. rate at un-
 steady regime in heavy
 water circuit of reac-
 tor A1

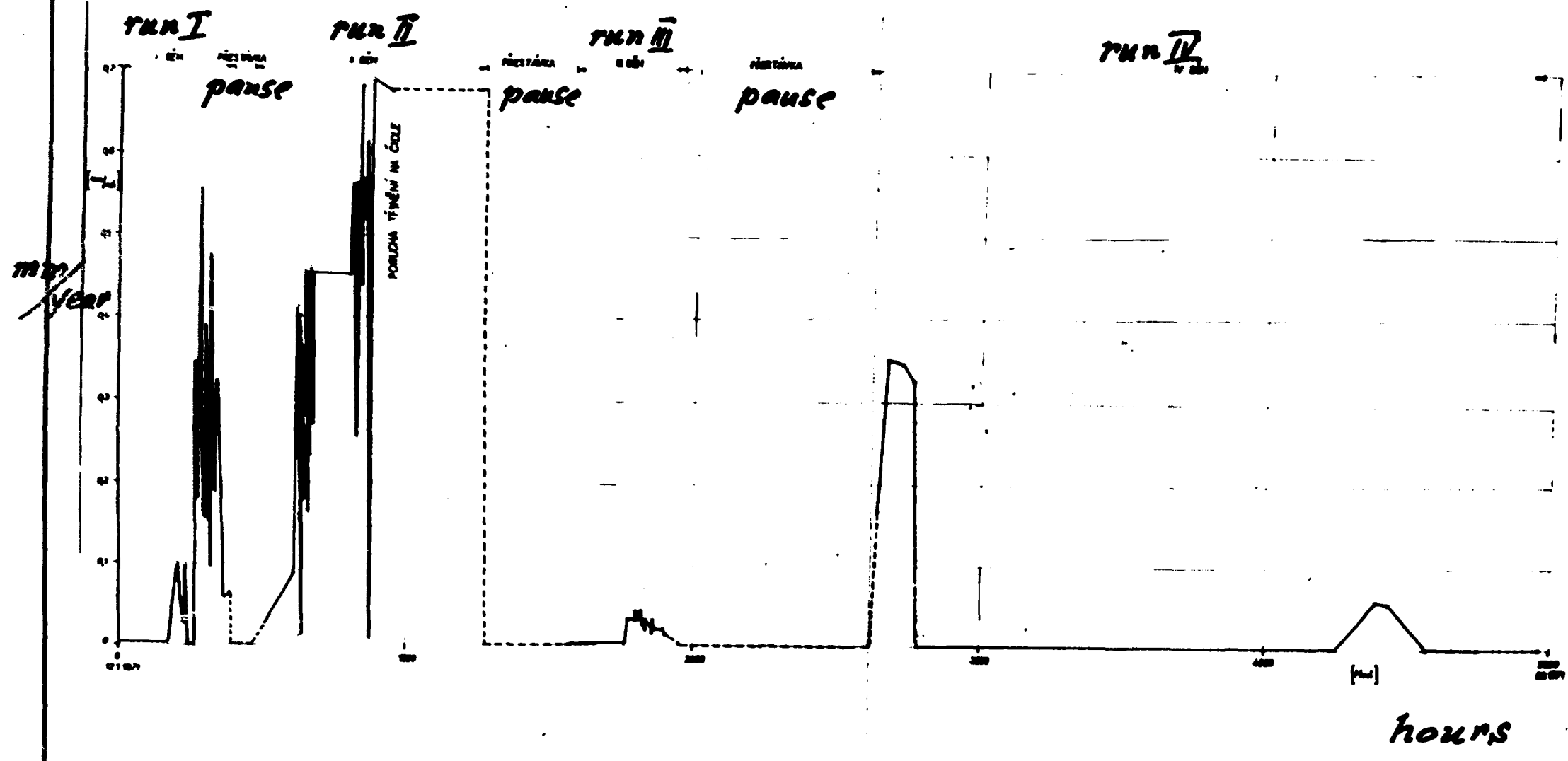
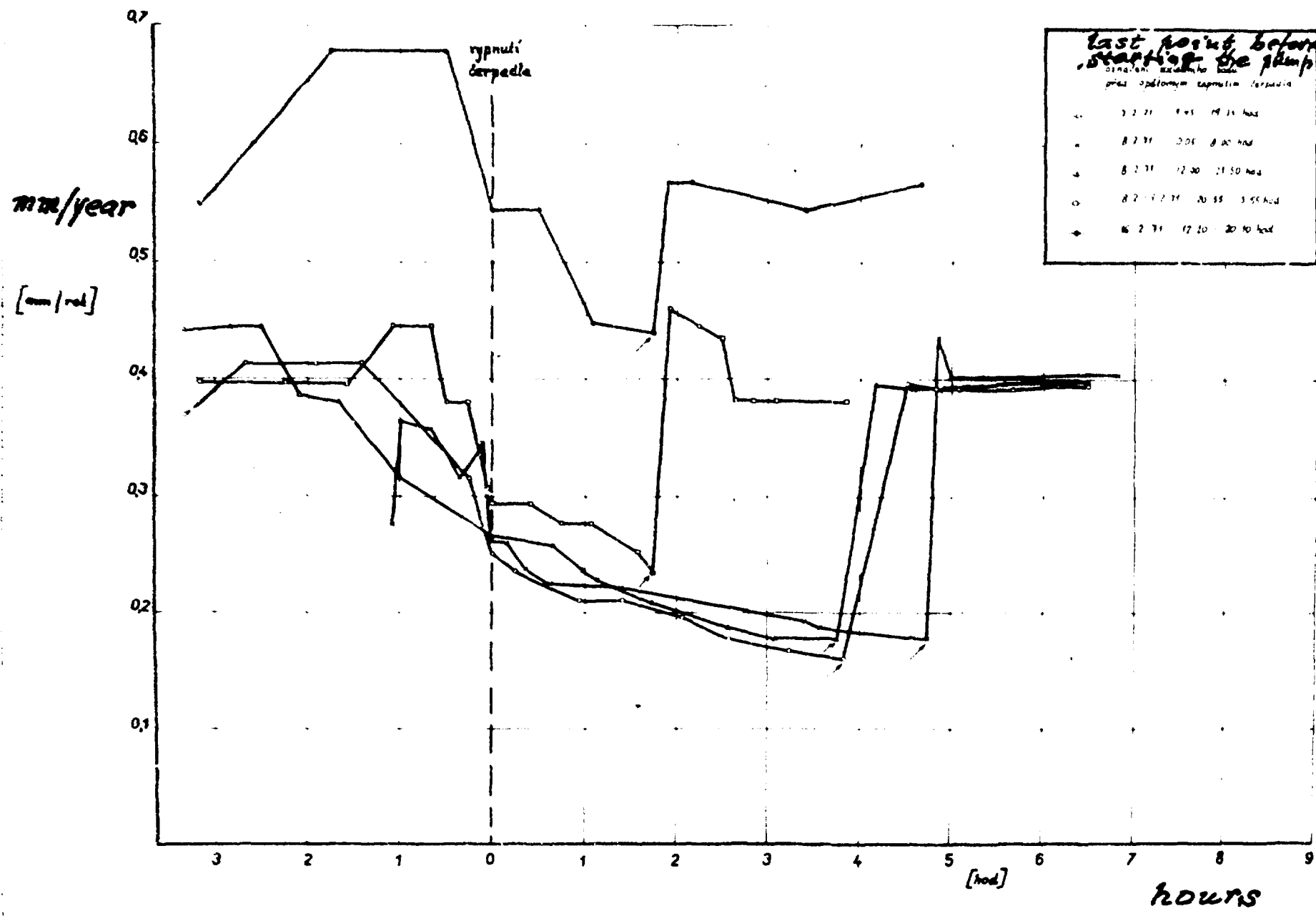


Fig. 17 : Course of the instantaneous corrosion rate of Al-Mg-Si type aluminium alloy during complex tests of Al-reactor



Priloha k tabuľke 10 - zmeny parametrov pri zapnutí čerpadla

oznacenie	pri zapnutí		po zapnutí	
	Prv (atp)	t (°C)	Prv (atp)	t (°C)
□	16,1	17	16,3	17
△	15,2	16	15,2	16
▽	16,8	16	16,4	16
○	16,9	17	16,9	16
◇	11,5	10	11,5	10

Changes in water parameters due to repeated pump starting

Fig. 18 : Influence of pump handling on the instantaneous corrosion rate

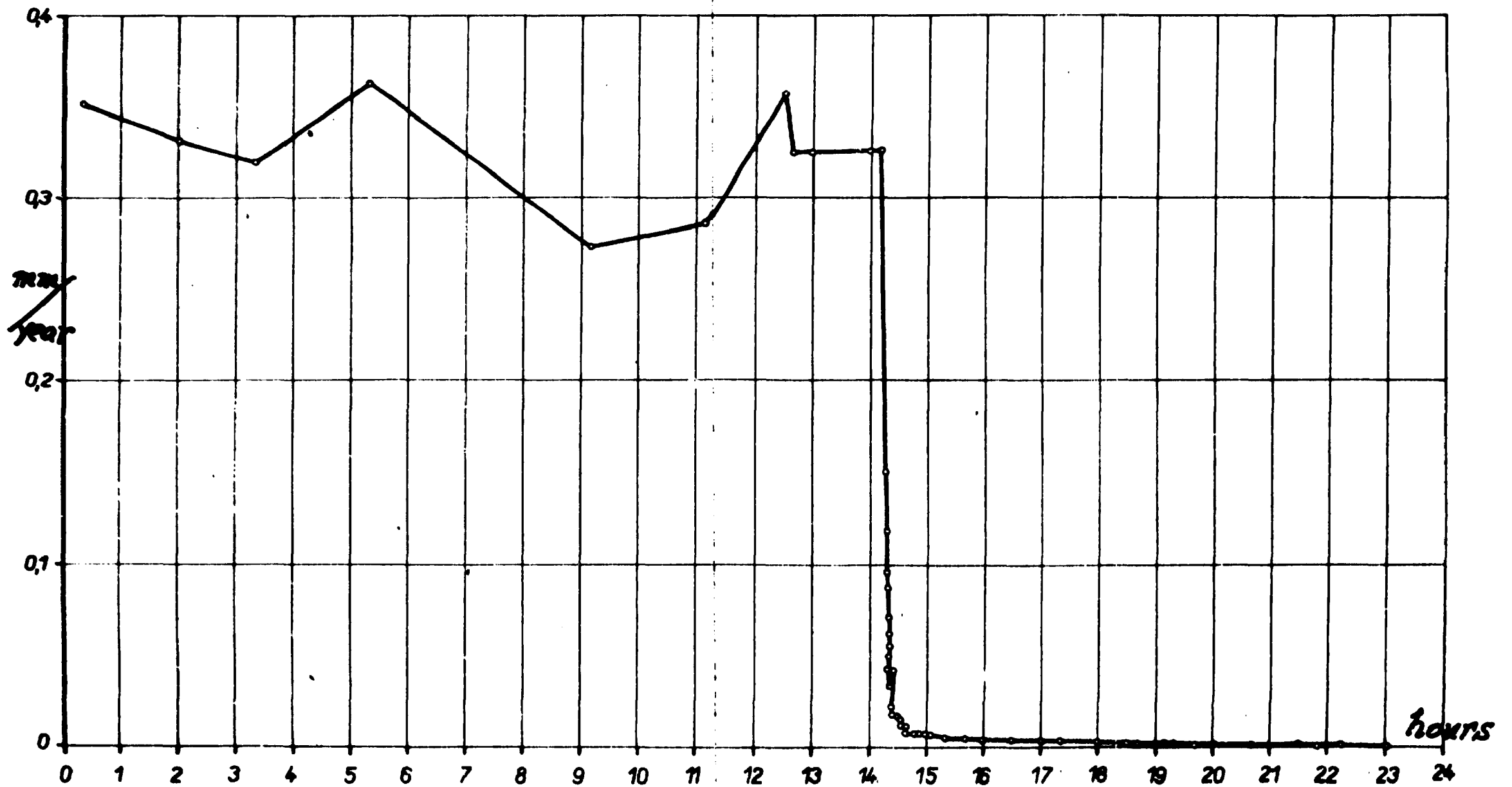


Fig. 19 : Influence of single-step charging of H_3PO_4 on the instantaneous corrosion rate of Al-Mg-Si type aluminium alloy