

CORROSION MONITORING AND CONTROL IN REFINERY PROCESS UNITS

Alec Groysman
Oil Refineries Ltd.
P.O. Box 4
31000 Haifa, Israel

Avihu Hiram
HIRAM - Process Control Eng. Ltd.
22 Martin Buber St
34861 Haifa, Israel
eMail: hiram@netvision.net.il

ABSTRACT

This paper describes the experience gained in "corrosion monitoring" in the overhead systems of three crude distillation units of a refinery in Haifa, Israel.

The data of electrical resistance (ER) probes, connected to an on-line data acquisition system were compared with the mass loss method and chemical analysis of accumulated sour water after condensation in the overhead system.

SEM & EDS analysis of films and deposits formed on the coupons showed that iron sulfide with impurities of chlorides are responsible for the corrosion extent. The corrosion was less than 5 MPY when a uniform tenacious iron sulfide films of 10-50 microns thickness were formed. The severe corrosion occurred when deposits and non-uniform films of more than 80-100 microns thickness were formed.

Special attention was given to ER probes which were connected on-line to the process units and enabled the operators to react immediately to any change in corrosion rates.

KEYWORDS: corrosion monitoring, crude distillation unit, mass loss method (coupons), electrical resistance (ER) probes, on-line corrosion monitoring system, Distributed Control System (DCS), accumulated condensed sour water.

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INTRODUCTION

Crude oil contains different species which while being processed reacted or converted into substances corrosive to alloys.

Water is condensed during the production processes and gases like hydrogen chloride (HCl) and hydrogen sulfide (H₂S) are dissolved in this water, various salts (chlorides, sulfides, hydrosulfides) and oxide-hydroxide deposits formed on the metal surfaces result in severe corrosion in the overhead system of the crude distillation unit. Air coolers, heat exchangers, condensers and pipes made of carbon steel suffer from general corrosion, pitting corrosion, and under deposit corrosion.

Prevention of corrosion damage and possible detrimental effects on the environment depend on knowledge of the corrosion situation at the units, that is "corrosion behavior" of metallic equipment, especially their corrosion rates and corrosion forms.

Various types of corrosion monitoring methods were recommended for follow-up in the overhead system of distillation units [1,2]. We did not find literature comparing the various types of monitoring results and how effective it is in evaluating real time corrosion.

SEM & EDS method is widely used for the identification of corrosion products [3], but we did not find in the literature, how this method is particularly used for the chemical identification of corrosion products and morphology of coupons' surfaces from the overhead system.

Given this apparent lack of well published basis for using various corrosion monitoring techniques, we attempted to use our practical experience to define ways how to utilize these tools to monitor Real Time Corrosion in the Equipment.

Corrosion follow-up in the overhead systems of three crude distillation units consisted of on-line monitoring with ER-probe measurements, long-term mass loss coupon measurements, visual examination of coupons, identification of deposits formed on coupons and investigation of coupons' surfaces by means of SEM & EDS, and chemical analysis of accumulated condensed sour water.

The collected information is analyzed by experts and conclusions are drawn as of the required changes in the anti-corrosion treatment program. The data, their treatment, the analysis and the conclusions are presented in a periodic report by the corrosion engineer to the management, to the operation people, to the maintenance and to the technical services. Some of the information is also presented in an on line information system and are made available to all concerning staff.

These also serve the goal of improving anti-corrosion measures, prediction of equipment service life, decision of needed maintenance and shut-down period.

EXPERIMENTAL PROCEDURE

A. MASS LOSS (ML) METHOD

Retractable corrosion probes with coupons were used. The mass loss of coupons made of a carbon steel (the same material the corrosion of which we want to monitor) strip specimen and their corrosion rates were measured every 40-60 days. The exposure period depended on the corrosion. In some cases, where the corrosion rate was too low to be measured, we had to extend this period up to 190 days.

After the retraction of the coupons, hydrochloric acid (5%) with organic corrosion inhibitor was used for cleaning coupons' surfaces from corrosion products and films. Analytical weighing was used for definition of the mass loss of the specimen.

B. ELECTRICAL RESISTANCE (ER) METHOD

Retractable ER-probes were used for measuring changes of electrical resistance of sensor made of carbon steel wire or cylinder and thus corrosion rate. The ER-probes were located in close proximity to the corrosion coupons, close to the wall of heat exchangers or pipes as possible. The measuring of changes in the electrical resistance of the sensor was done by portable device or continually monitored by an on-line monitoring (acquisition) system.

The corrosion rates were calculated from the slope of line "Dial reading of ER-probe versus Measuring time".

The on-line monitoring included also data collecting system, calculations, performing and utilization of received data.

C. CHEMICAL ANALYSIS OF ACCUMULATED CONDENSED SOUR WATER

The chemical analysis of corrodents (pH, chlorides, sulfides, sulfates) and corrosion product (iron) in accumulated water was carried-out five times a week by means of conventional laboratory methods. The data of pH measurements under laboratory conditions were compared with on-line pH-meters which are mounted in the process streams as part of the operating monitoring and control system. The data obtained in the laboratory were also made available to the technical team.

D. VISUAL EXAMINATION OF COUPONS

Visual inspection of coupons' surfaces was done every 40-60 or 190 days, after removing from the places of their mounting in the system.

The presence of film and deposits formed on the coupons' surfaces, their uniformity, pits or other corrosion phenomena or damages were described.

The film and deposit thickness on the specimen was measured by means of special device for measuring non-conductive or non-magnetic films on the iron. Some expertise and experience needed in order to make out the important facts which should be considered in the anti-corrosion efforts.

E. THE IDENTIFICATION OF CORROSION PRODUCTS ON THE COUPONS

The chemical composition of corrosion products, films and other deposits formed on coupons' surfaces as well as morphology of these surfaces after removing of deposits was analyzed by means of SEM & EDS. The device JSM-5400 of JEOL was used for these purposes.

RESULTS AND THEIR DISCUSSION

The arrangement of corrosion probes in the overhead systems of a typical crude distillation units is presented in Figure 1. The general scheme of corrosion monitoring logic, the relationship between its various methods and its possibilities are described in Figure 2.

I. CHEMICAL ANALYSIS OF ACCUMULATED SOUR WATER

The chemical analysis of accumulated sour water formed after condensation of overhead gases from the atmospheric distillation columns, has been used for many years to make out the details about corrosion "behavior" in the overhead systems. The chemical analysis of the corrodents (pH, chlorides, sulfides, sulfates) and the corrosion product (dissolved iron mainly) give relatively fast and reliable "picture" of both sides of the corrosion system. These data facilitate improving neutralization and inhibition treatment in the overhead system and improving the desalting process of the crude.

The chemical data of accumulated sour water do not reflect exactly the real corrosion situation in the overhead system. The first reason is that the most vulnerable place from the corrosion point of view is situated in the air coolers and condensers - heat exchangers where the shock condensation is taking place (see Figure 1). It is clear that there are differences between pH, corrodent content in the overhead (in the place of shock condensation) and below in the accumulated water drum (the water sampling place for the chemical analysis). The second reason is that the iron content in sour water does not always reflect real corrosion situation. For example, iron sulfide formed on the surface of carbon steel may dissolve as a result of pH changes or concentrations of other species and not as a result of a corrosion process.

The chemical data enable the indication of corrosion situation and general information in the overhead system. It is acceptable to run the system with pH values of 5.5-6.5 subject to chlorides and iron content lower than 20 ppm and 0.5 ppm respectively. Information about corrodents and corrosion product content enable improving anti-corrosion treatment.

High changes of pH values as well as content of chlorides and iron in sour water indicate an unstable conditions in processing and as a result bad corrosion "behavior". In spite of this, there is no information about the real corrosion rates and the actual corrosion forms. There is no way to forecast, from the chemical analysis of the sour water only, the tube service life and shut-down periods.

The chemical method gives qualitative rather than quantitative information of the corrosion situation. Therefore the metal loss coupons, visual examination, identification of corrosion products and films and ER - probes were utilized to complete the "picture" of the corrosion in the overhead system of the crude distillation units.

II. MASS LOSS (ML) METHOD

This method is described in literature [4,5]. There is no universal method for corrosion follow-up. Every method has advantages and disadvantages, limits and benefits. Mass loss method enables measuring the average corrosion rate over a period. Visual inspection enables defining the presence of deposits and pits. The salt deposits on the coupon surfaces shows the necessity of increase washing in the overhead system.

Chemical identification of films and deposits formed on the surface specimen enables ascertaining corrosion mechanisms, that is the causes of corrosion process and thus diminishing or preventing its spreading.

The results of mass loss method corrosion follow-up that have been collected for the last two years are presented in Figure 3.

The strip coupons show the corrosion situation only in the places of its mounting. The corrosion situation may differ in the other places of the system. Therefore the more coupons we insert in the overhead system the better "picture" we are going to get of the real corrosion situation.

The exposure period of coupons depends on the expected corrosion rate values. There is no sense in taking measurements and hence having no meaningful value when the corrosion rates are too low to determine. The exposure period for coupons was first set to 30 days and then extended up to 60 days and 190 days when corrosion rates were low (thousandths and hundredths mm/y), in order to receive reliable and correct data. The obtained data show that corrosion rate of carbon steel before the air cooler is higher than after its heat exchangers (see Fig. 3).

This fact indicates that condensation occurs before air cooler.

One should note that corrosion rate in some cases is twice the permissible value (accepted, dangerous or limiting). This permissible corrosion rate was determined as 0.11 mm/y (5 MPY) for the carbon steel tube bundles of air coolers, heat exchangers and condensers. It is very important to achieve a correct interpretation of mass loss coupon

data. The thickness of tube bundles in many cases is 2.336 mm. The planned life of air coolers, condensers and heat exchangers in refineries is 15 years [6]. Thus the accepted or permissible corrosion rate for this equipment is:

$$0.7 * 2.336 \text{ mm}/15 \text{ y} = 0.11 \text{ mm/y (5 MPY)},$$

where 0.7 - wear and tear coefficient, that is the maximum percent (70%) that thickness of tubes are allowed to be diminished up to its replacement. It means that corrosion rate up to 0.11 mm/y is acceptable.

This value coincides with the one NACE recommendation as an accepted low corrosion rate for the equipment in the oil industry [4].

SEM & EDS analysis of corrosion products and films formed on coupons

In addition to corrosion rate values, coupons enable defining corrosion form and mechanism based on surface state (morphology) and chemical identification of films and corrosion products formed.

General corrosion with uniform films, and pitting corrosion under non-uniform films and deposits have been found.

The analysis of corrosion products made by means of SEM & EDS, showed the presence of iron, sulfur, oxygen, small quantity (traces) of chloride and sometimes even bromide (Figures 4,5).

The obtained data point out that iron sulfides (probably FeS and some other forms Fe_xS_y) covering the carbon steel surface are responsible for the formation of protective film.

The presence of nitrogen in the films is problematic because of its likely small quantities and close energy with oxygen atom. The presence of nitrogen suggests a possible inhibitive film formation by means of filming amine. The chloride alkaline salts are generally water soluble. In spite of this, traces of chlorides were found in the deposits and films (see Figure 4). The presence of bromides in the deposits in some cases (see Figure 5) may be explained by the usage of ballast tankers with sea water during the transportation of crude oil.

The pits formed under films and deposits on the coupons' surfaces can be explained by the presence of non-uniform iron sulfide film or ammonium and amine chloride deposits. If this film were perfect, uniform and tenacious not more than 50 microns of thickness, the corrosion was less than 5 MPY (0.11 mm/y).

When deposits and non-uniform films of 100 microns and more were formed, the coupons, arranged in the air cooler and condensers were severely corroded. Generally pits

were formed under non-uniform films and deposits. The iron sulfide film is cathodic to iron. If this film were perfect, the galvanic pair does not work, therefore corrosion is negligible. If this film were non-uniform and imperfect, the corrosion agents ingress in imperfections and severe pitting corrosion occurred under films.

The presence of ammonia or amines and chlorides in the overhead system results in the formation of ammonium and amine chloride deposits which may hydrolyze with formation of hydrochloric acid under deposits.

The pH values decrease to 2-3 and results in corrosion under deposits and in its turn pitting corrosion. The corrosion rate under deposits can be as much as 100 times as the general corrosion rate. In order to prevent the formation of these deposits, ammonia usage is minimized and generous water wash is applied. The deposits consisted of chloride salts on the coupon surfaces is an indicator of wash quality.

In cases where the deposits and sediments were consisted of iron sulfides, water wash could not be effective, because the sulfide salts are not water soluble.

The mass loss method has some limitations.

Corrosion coupons examination are unable to differentiate between long term steady corrosion rates and corrosion which has occurred rapidly over a short period of time, due to upsets or other events.

This method gives the overall average corrosion rate during some, usually long period. If corrosion rate was low (thousandths mm/y), the exposure time should be prolonged up to as long as half a year and it is impossible to retrieve any data during all this very long period.

The other deficiency is that a lot of time has to be spent for preparation of coupon specimen surfaces before and after exposure, and for calculations. Not every one can use this method and highly skilled and well trained people are needed to get meaningful data.

The use of ER-probes overcomes most of these drawbacks.

III. ELECTRICAL RESISTANCE (ER) METHOD

A. Manual registration method.

Retrievable ER-probe was mounted parallel to mass loss coupons in the overhead system of the crude distillation unit. A portable device was used for registration of the changes of wire sensor electrical resistance [7]. Corrosion rates were calculated according to slope of an average line "dial reading of ER-probe - exposure time" (Figure 6).

Curve fitting by regression analysis was carried out for the data received from this device.

ER-method gives results considerably quicker, and less efforts are needed in comparison to the mass loss method.

Properly selected ER-Probes enable data to be read close enough to give instant information about events in the "ER-probe life". The various results may be received for the different periods (Figure 7). Phenomena like sudden reversing the corrosion process might be indicated: R values go to the opposite direction - decreasing (Figure 8). Finding reasonable explanation for this phenomena is always problematic. One of the explanations for such fluctuations is that protecting films on the sensor surface are formed and destroyed periodically. Another possibility is the periodic formation of films with various electrical conductivity. If the measuring period taken is long (the same period as for mass loss method) then identical results are received.

As a rule the corrosion rates are lower when measuring periods are longer (see Fig. 8). The similar results may be received by means of the mass loss method. When the exposure period of coupons is increased the average corrosion rate is diminished. Generally this relationship occurs when dependence of specimen mass loss versus time is described by a curve with "saturation" (Figure 9). This phenomenon often occurs when carbon steel is under neutral or near neutral solutions. Comparison of the results received by means of two methods, mass loss and ER, during long-term periods shows their full conformity (Figure 10).

B. On-line corrosion monitoring.

A number of ER-probes with 4-20 ma output as a function of R changes were installed in the overhead of two crude distillation units (see Figure 1). The installation of these devices gave us the ability to measure and monitor the corrosion rates in and around the places they were mounted at, to get accurate - real time feed back data about the process and from the anti-corrosion measures taken - all these to reduce the time needed to react to changes in the plant (processing) and to minimize the corrosion damages.

ER-method is one of the corrosion monitoring ways which better enables operators to know the exact and real situation of the equipment with regards to the corrosion and decide quicker how to improve the treatments such as desalting, maintaining the right process conditions and the right parameters of the anti-corrosion program: injection of soda and other types of neutralizers, inhibiting agents etc.

The philosophy of on-line ER corrosion monitoring includes the data collecting system, their treatment (performing the calculation), utilization the data and their interpretation.

The analog signals (4-20 ma) are sent from the probe are proportional to the un-corroded matter left and are calibrated to give an indication of total corrosion of the steel sensors in microns.

The outputs of these probes are monitored via the existing DCS (Honeywell/TDC3000) and are also sent to the Plant Information System (PI) where they are analyzed. Figure 11 shows these data as collected and stored within the PI System. The PI System enables easy access to the history data base with every simple PC which is connected to the local net or by dialing-in from remote PC's. Bringing this information onto the PC makes possible the manipulating with all kind of analysis tools not only from within the PI System but from outside it on other systems which might be available on any PC in the network (e.g. commercial available spreadsheets and various statistical software).

Performing the calculations. Based on the field instrument readings corrosion rates are calculated by means of differentiation of received data regarding given period. In order to make meaningful calculations it is essential to first filter the noise from the data. A number of approaches were practiced.

The simplest way is to take all the readings that were collected within the Information System and find the regression line which best fits the data (Figure 12).

Another technique which is more suitable for on-line calculations is filtering by averaging over periods of time and making the corrosion calculations between separated averages. There are two parameters to adjust in the application of this algorithm: the length of the period to be averaged to give representing values and the time to separate between these two values (Figure 13).

The calculated corrosion rates are depended on measured period, and these data are presented for various periods (Figure 14). The title of each trend indicates how many hours were averaged and what is the distance in time between these averages. The calculation was done continuously and the results were stored in the system history.

Long periods (longer than 30 days) give integral corrosion rate values coinciding with the data of mass loss method, but the latter does not allow to follow changes in corrosion as it happens during this period. On-line ER data allow analyzing during various small periods (Figure 14). These data reflect process changes as it reflects the corrosion and enables the experts to find the reasons for these upsets and to try to improve or eliminate the causes and minimize the corrosion damages.

4. Actual Equipment Inspection Data

After four years of service actual equipment inspection of heat exchanger tubes was taken at planned turnaround.

The tube bundles in the overhead atmospheric unit are under reduction conditions (H₂S atmosphere) during normal operation. When the equipment is opened for inspection they are exposed to normal atmosphere (with oxygen), and oxidation processes immediately take place. The black deposits of iron sulfide inside the air cooler becomes reddish iron hydroxides within several hours after opening of the cooler. Therefore it is important to have the inspection of the tube bundle done as soon as it is opened to the atmosphere. Visual examination had been done immediately after opening the heat exchangers. The tubes were found to be covered with black deposits of various thickness. The chemical analysis showed the deposits consisted of iron sulfides and iron oxides. These deposits were removed by water jet, and tube surface was then visually inspected.

The general condition of the tubes' surfaces was good, but shallow pits of various size were discovered under the thick deposits. The pits on the tubes were very mild and of no dangerous for the on going service of the heat exchangers. These pits required no special attention and no specific action to be taken.

The actual equipment inspection findings matched the available on line monitoring data.

The ability to react fast to the signals given by the on line monitoring system enabled the anti-corrosion program to be adjusted in real time and helped to maintain the equipment under good service conditions.

CONCLUSIONS

1. The experience of corrosion monitoring in the overhead system of the crude distillation units in the refinery has been described.
2. Mass loss coupons and ER-probes showed good coincidence.
3. On-line, real time ER monitoring with data acquisition system, data analysis and calculations allowed following the corrosion and to react immediately and accurately to minimize the damages.
4. The combination of these methods enabled anti-corrosion program included crude desalting, neutralization and inhibition, to be optimized, to be more precise and more efficient. With these data it is possible to better predict tube service life and to plan the maintenance shut-down periods.
5. SEM & EDS analysis showed that iron sulfide films and deposits of variable content were formed on the coupons installed in air coolers and condensers in the overhead of the atmospheric columns.
6. The corrosion was less than 0.11 mm/yr (5 MPY) when a uniform tenacious iron sulfide films of 10-50 microns thickness were formed. The severe corrosion occurred

when deposits and non-uniform films of more than 80-100 microns thickness were formed.

7. The actual equipment inspection findings showed general good condition of tubes bundles and thus matched the available on line monitoring data.
8. The availability of on-line corrosion monitoring system enabled better look after anti-corrosion treatment and made the overall program much more successful.

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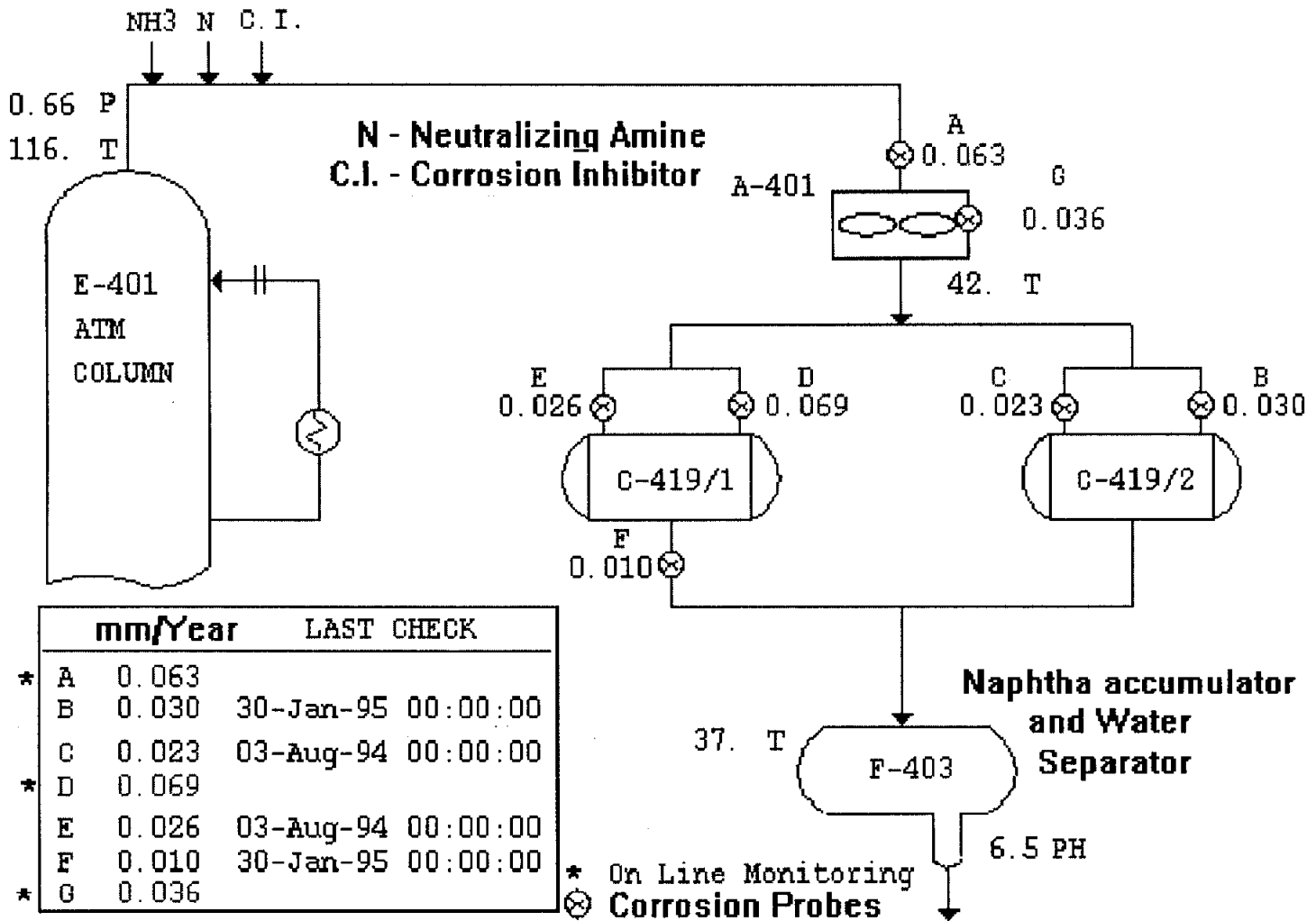


Figure 1 . Atmospheric overhead corrosion monitoring system

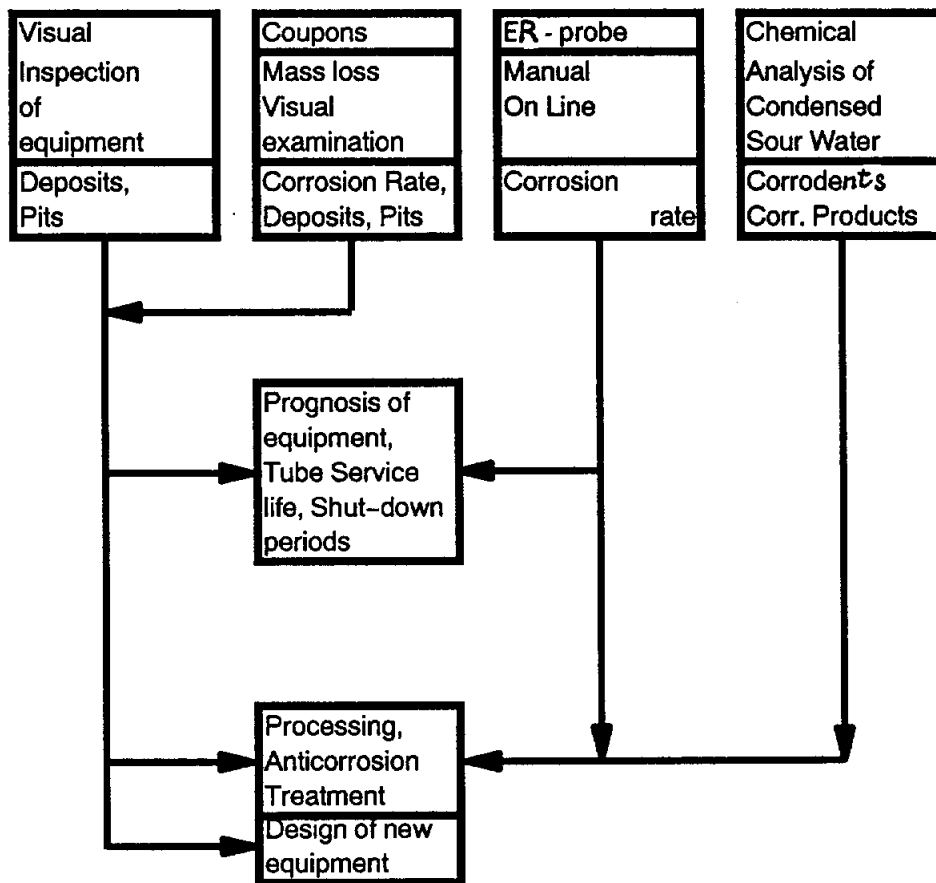


Figure 2 . Scheme of corrosion monitoring.

Corrosion Rate, mm/y

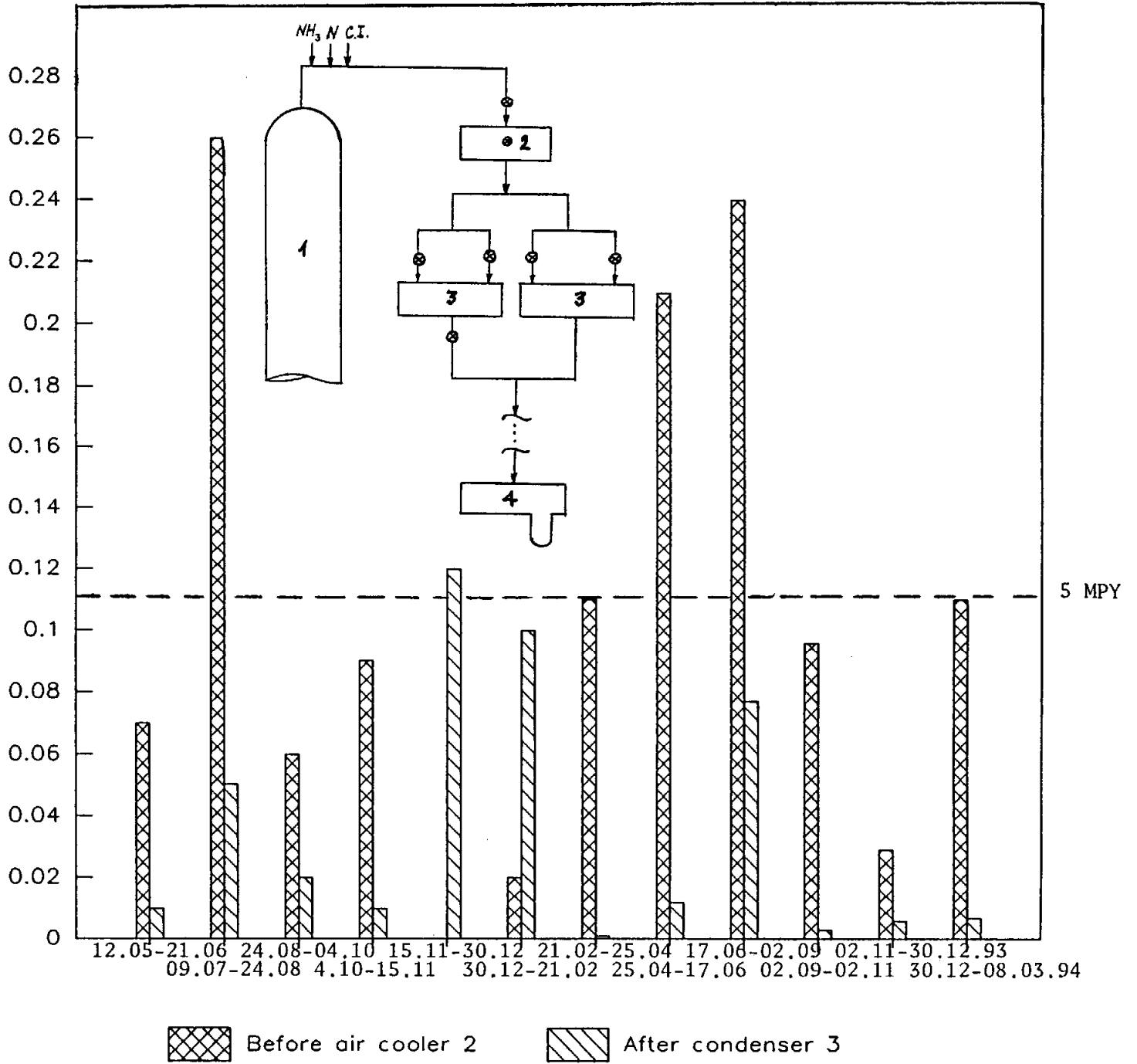


Figure 3. Corrosion rate vs time.

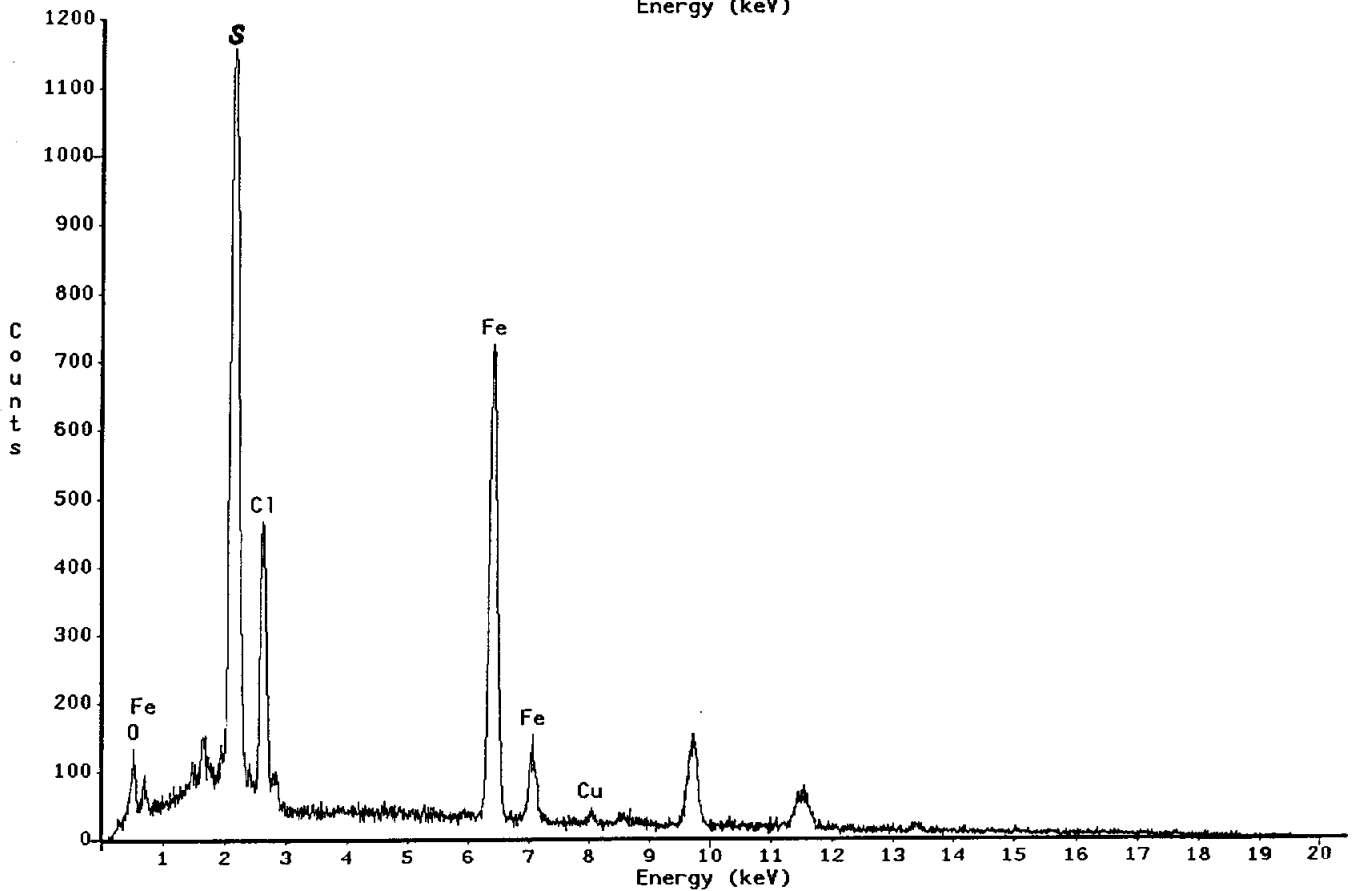
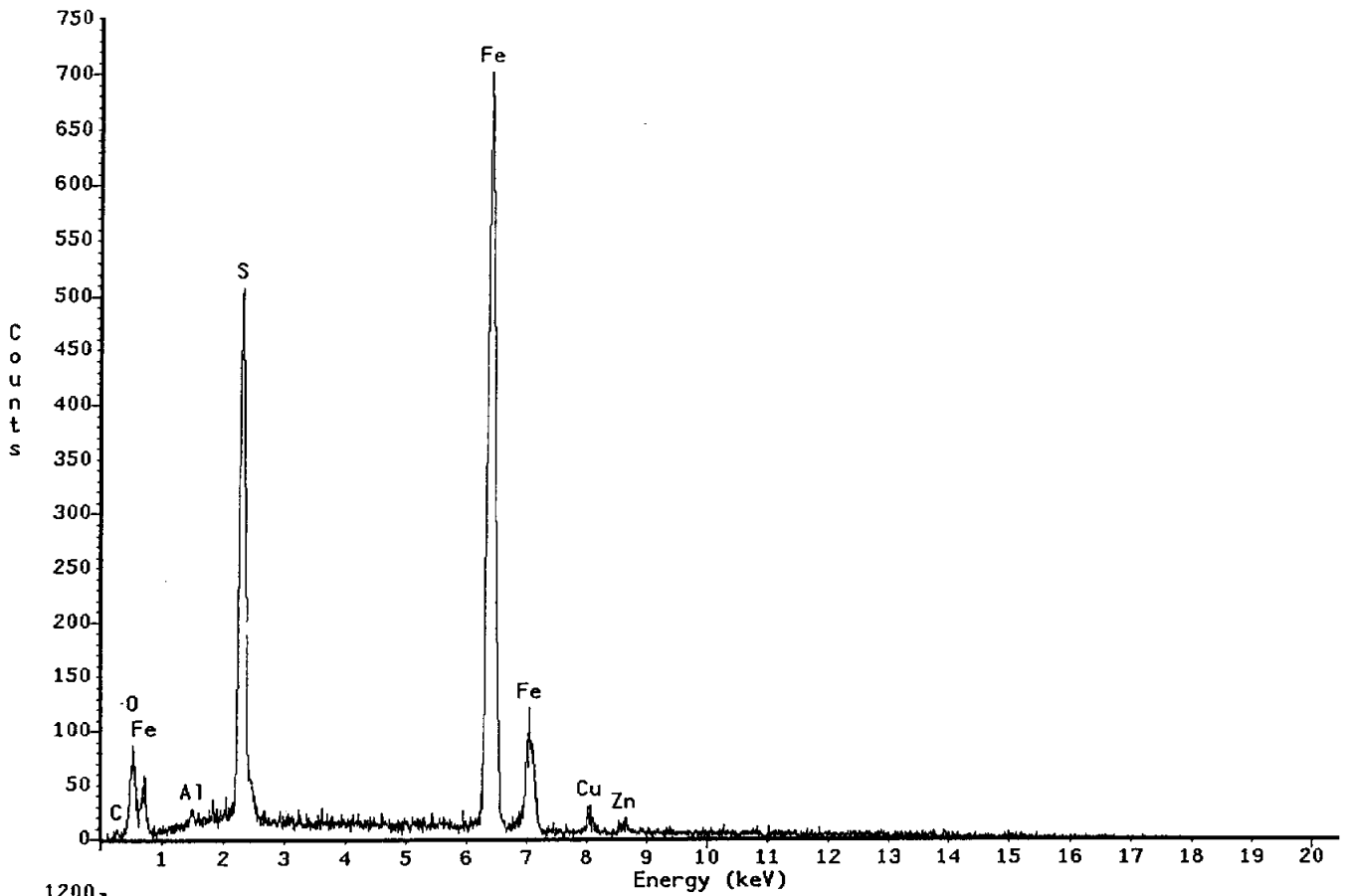


Figure 4. EDS spectra of film on coupon (a) and sediments (b) inside of air cooler.

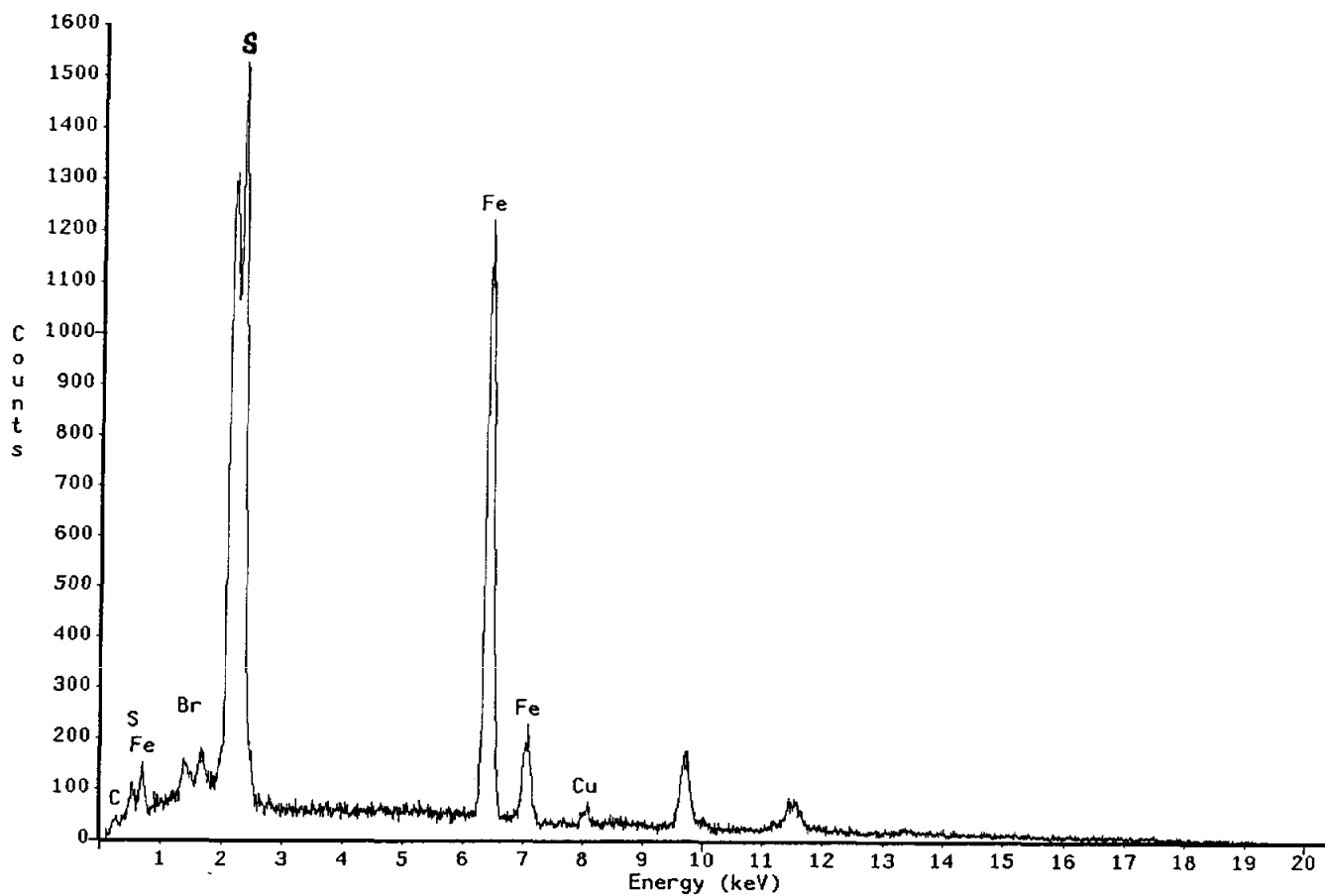


Figure 5. EDS spectrum of film on coupon after air cooler.

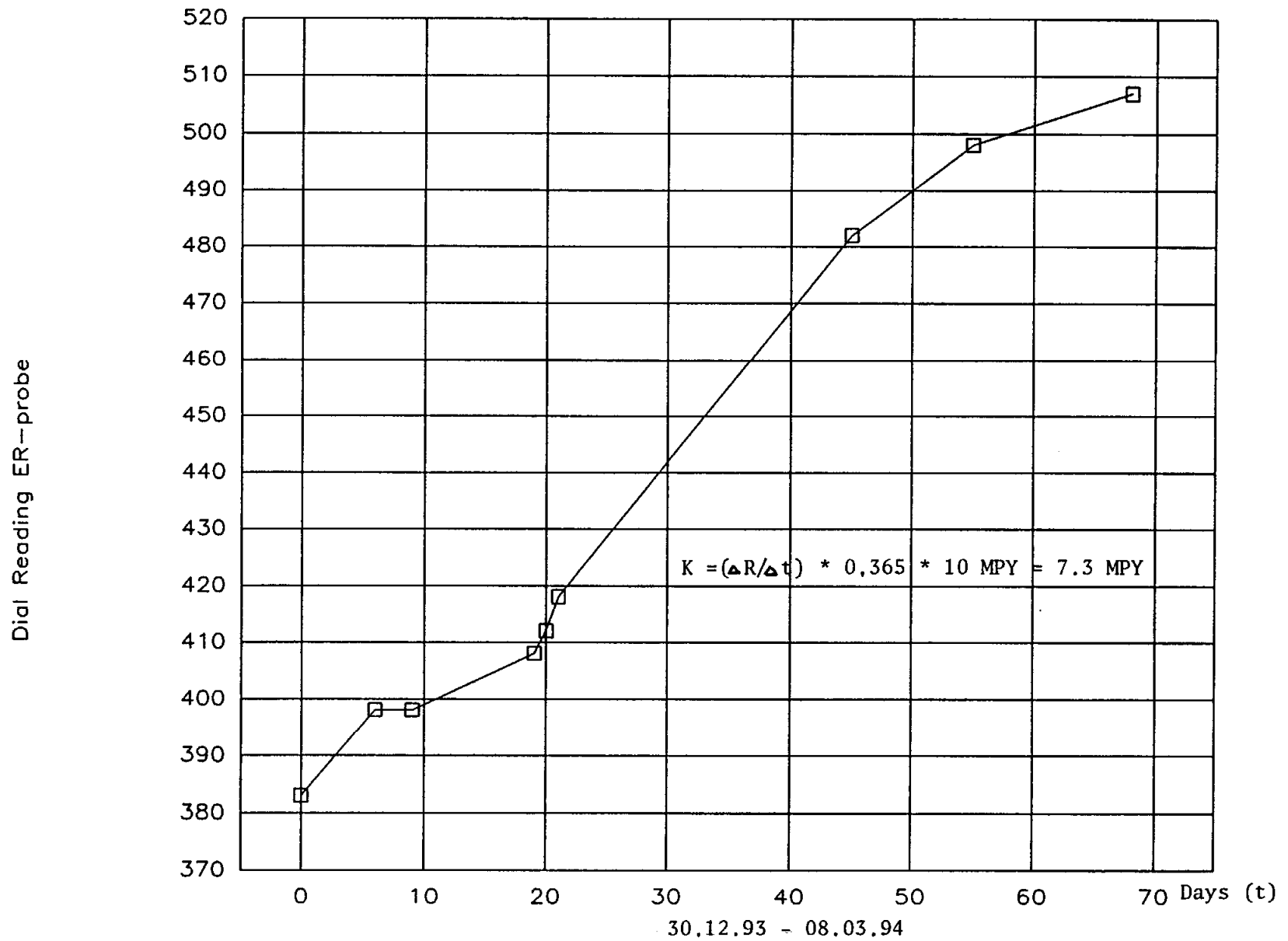


Figure 6. Dial reading ER-probe vs time.

Dial Reading ER-probe

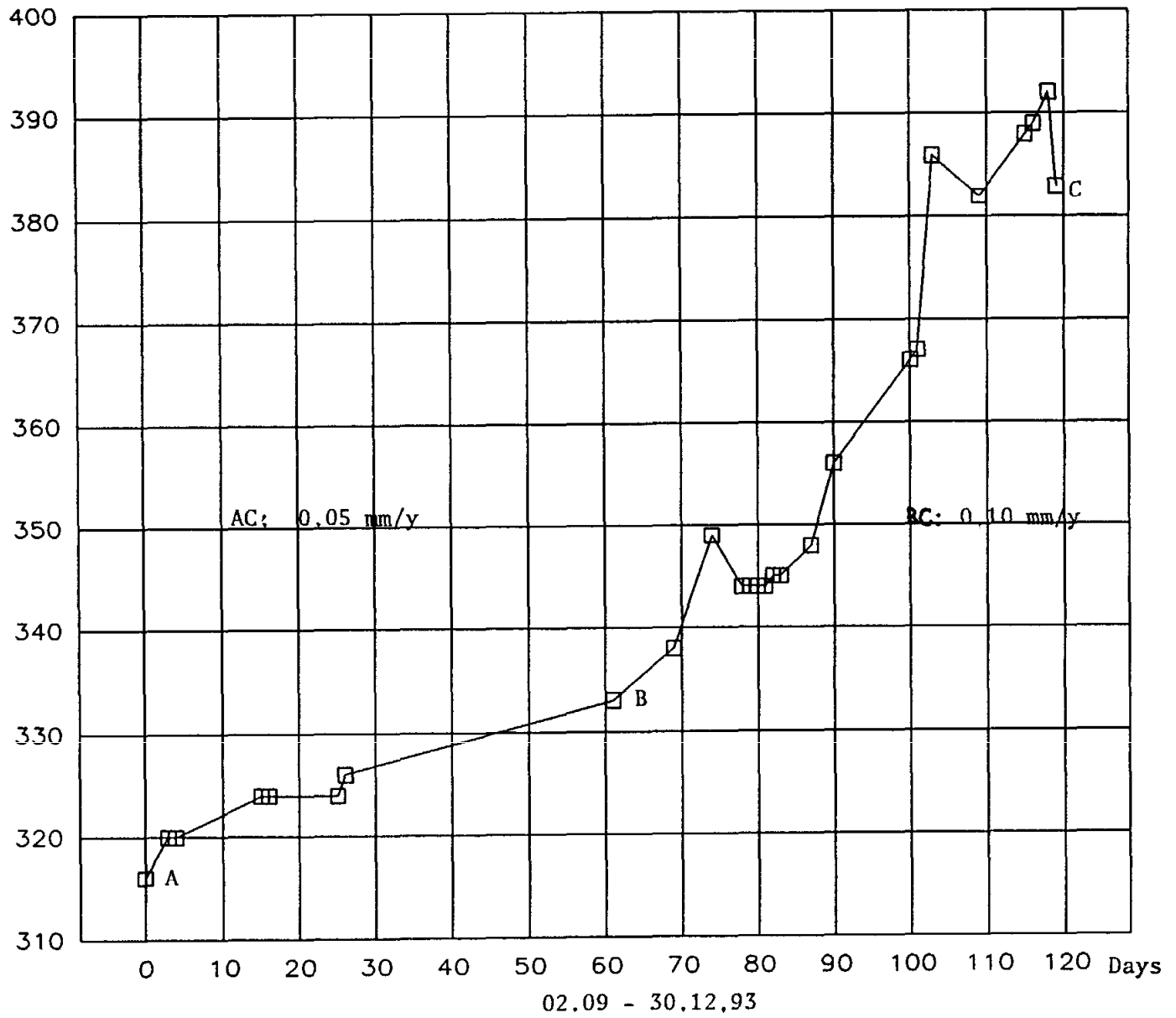


Figure 7. Dial reading ER-probe vs time.

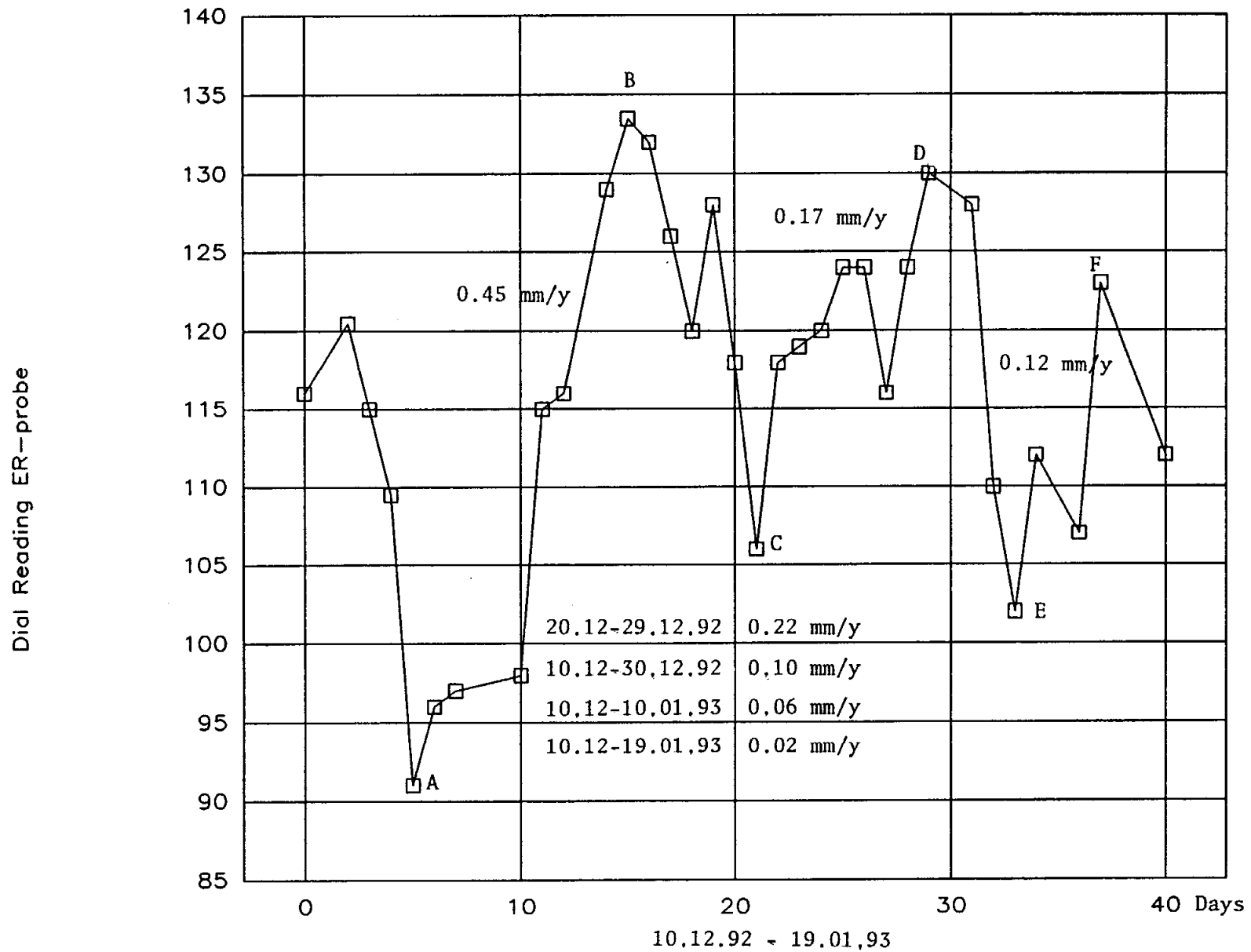


Figure 8. Dial reading ER-probe vs time.

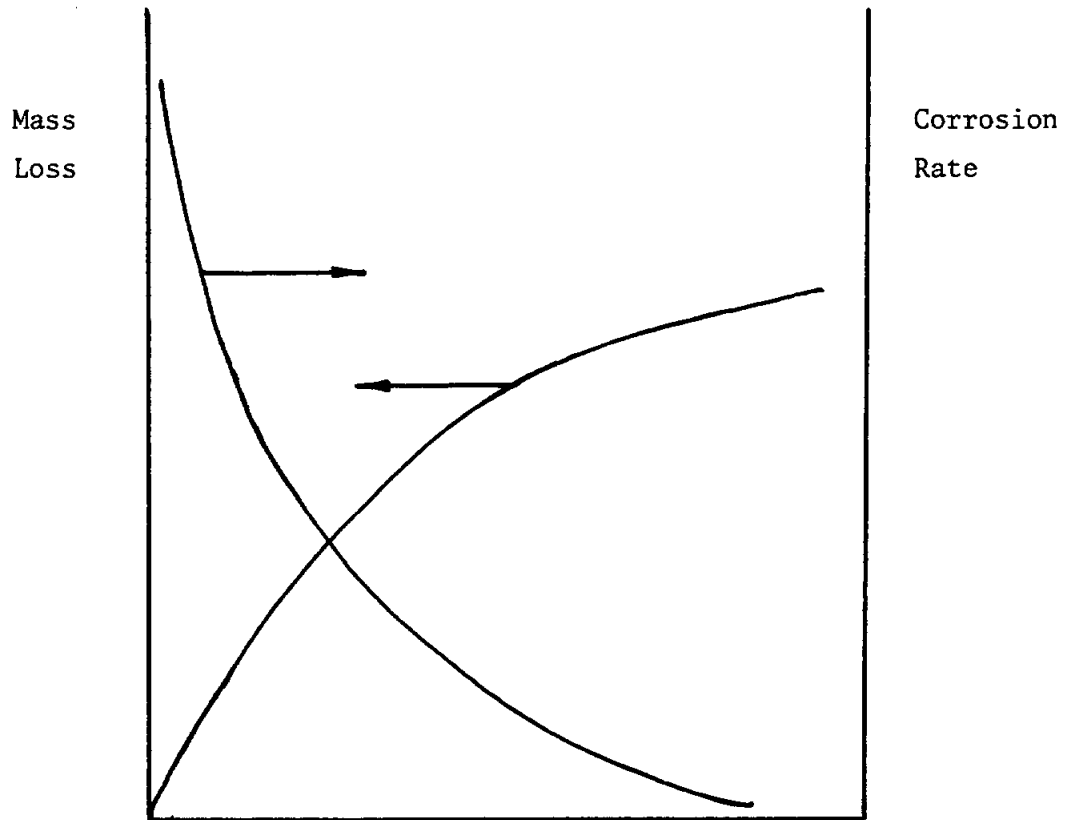


Figure 9. Mass Loss and corrosion rate vs exposure time.

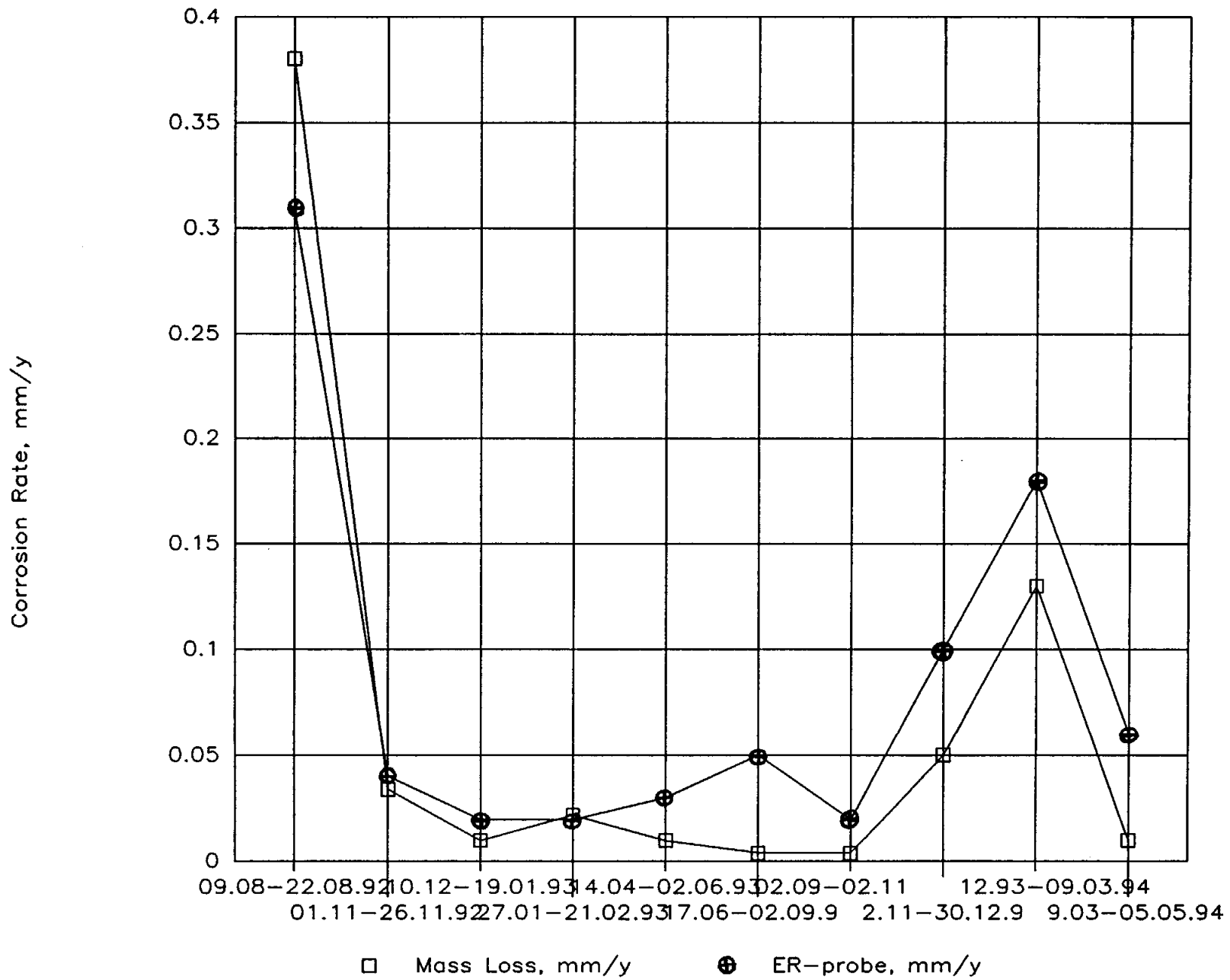


Figure 10. Corrosion rate (two methods) vs time.

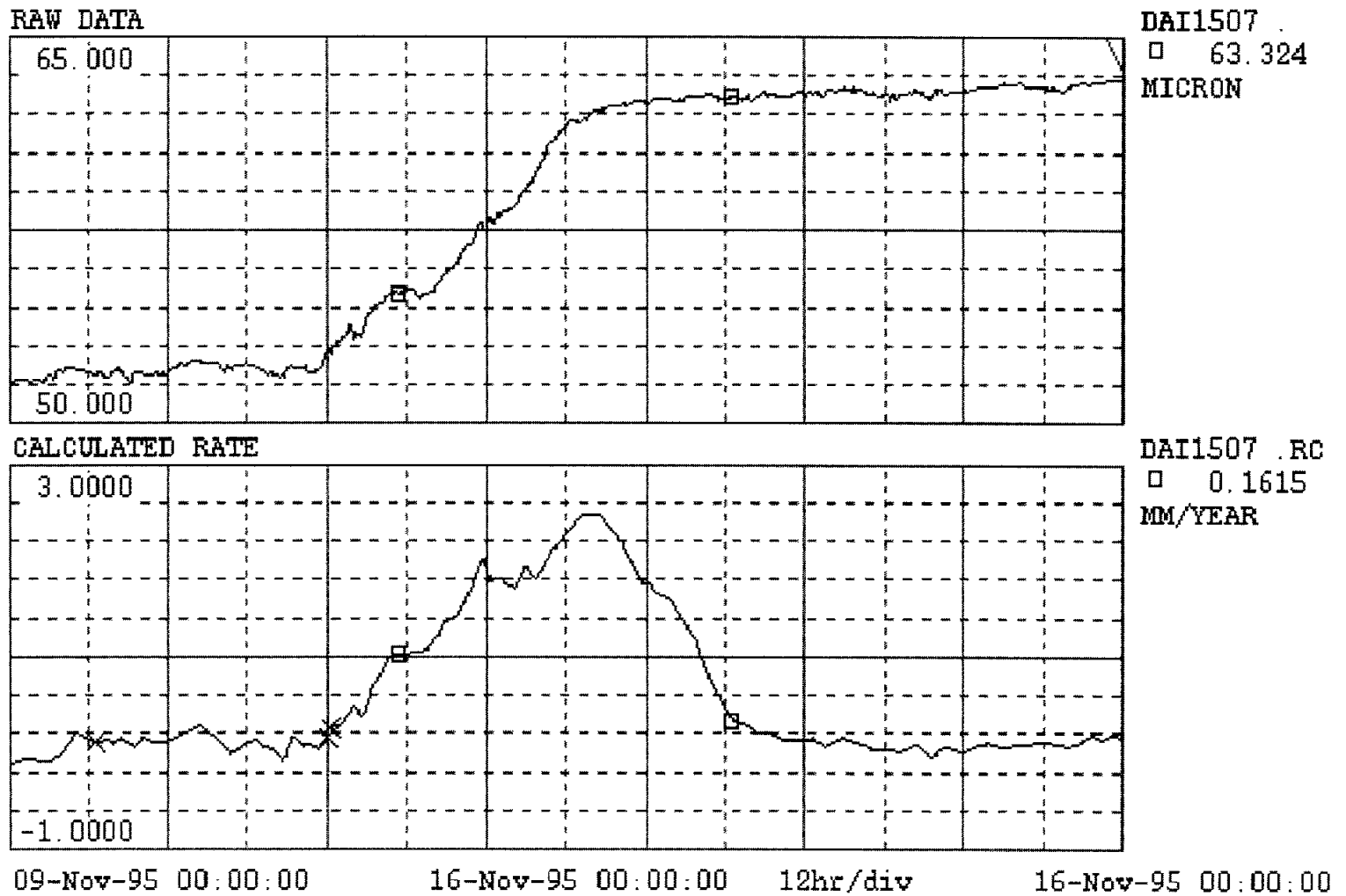


Figure 11 : Dial Reading and Calculated Corrosion Rate

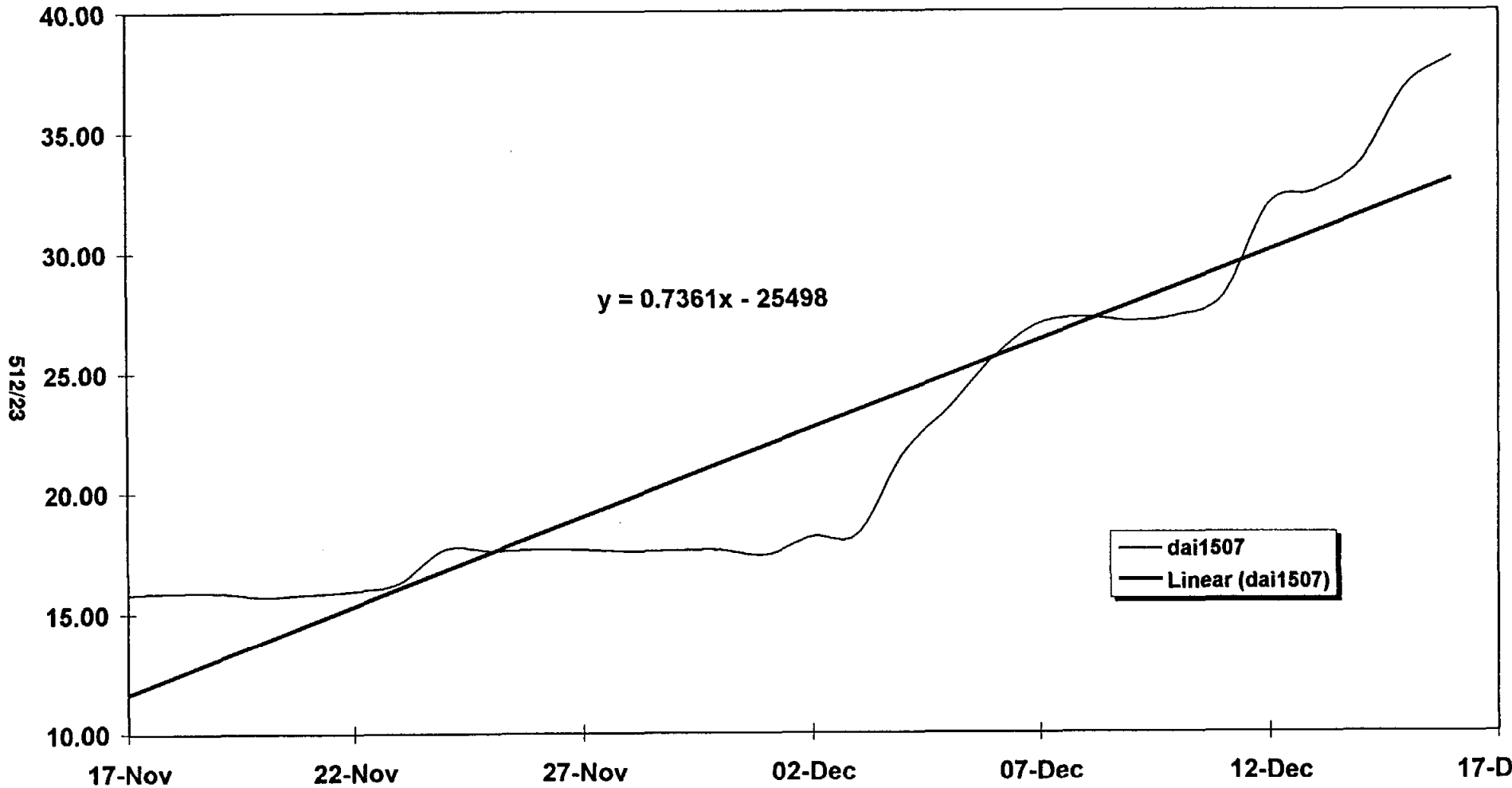


Figure 12. Dial reading and linear regression.

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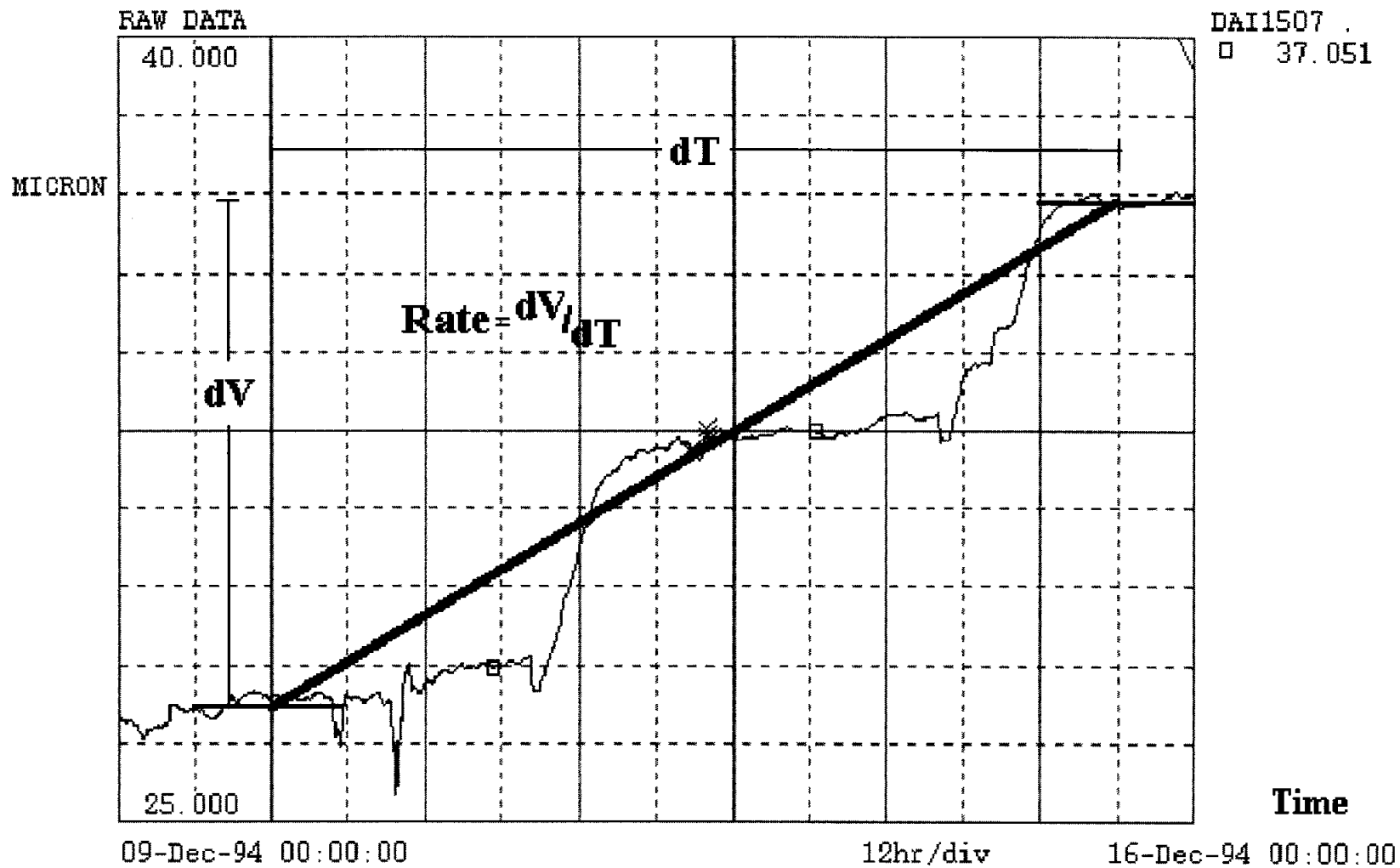


Figure 13 . OnLine corrosion rate calculation

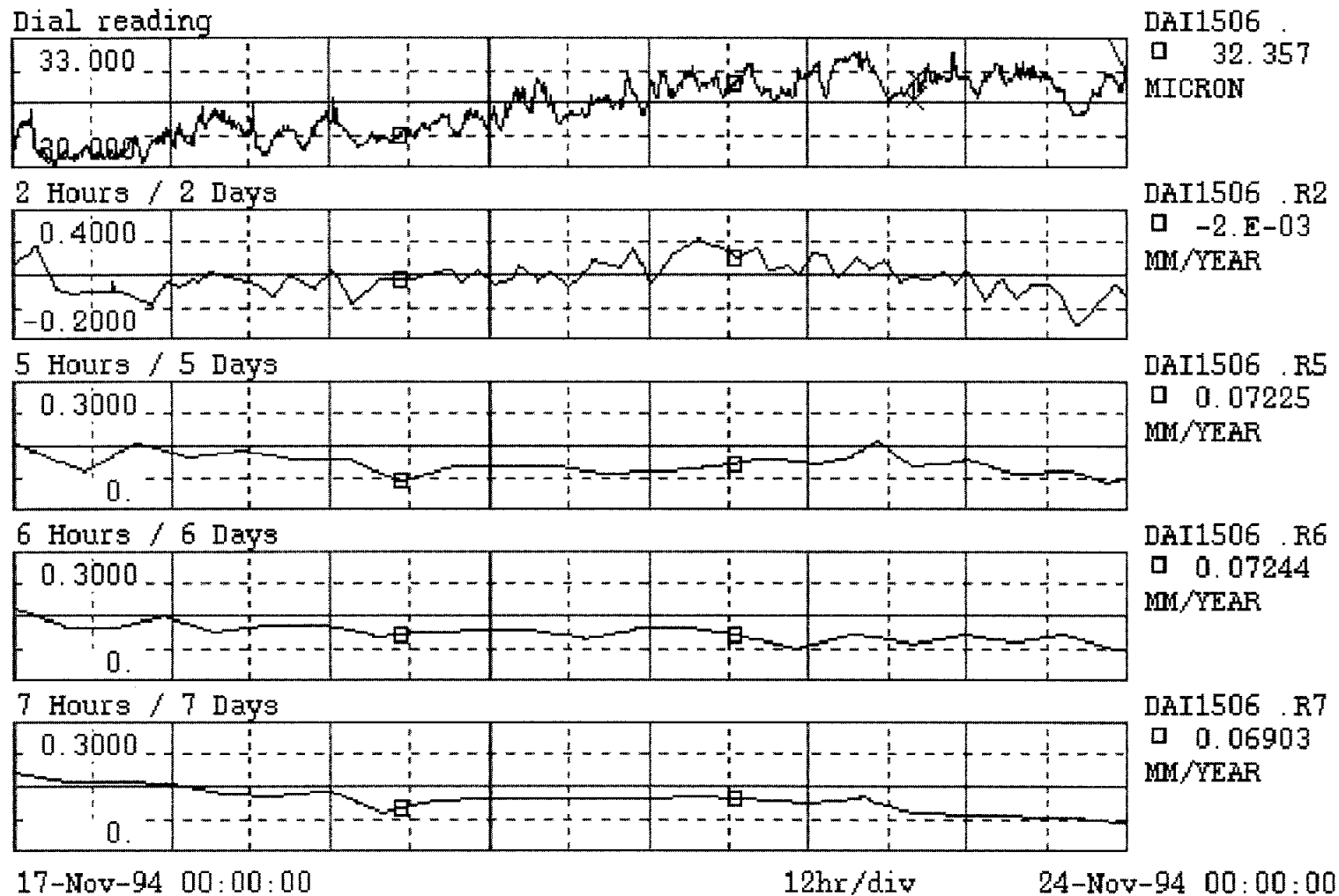


Figure 14 . Corrosion rate vs Time base