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FP 7 EURATOM Collaborative Project
“Redox Phenomena Controlling Systems”

Marcus Altmaier, Xavier Gaona, David Fellhauer,
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Foreword

The outcome of the CP ReCosy InterComparison Exercise is presented. The exercise was conducted within the EURATOM FP7 Collaborative Project "Redox phenomena controlling systems" (CP ReCosy). It took place 16-20 November 2009 in Karlsruhe, hosted by "Institut für Nukleare Entsorgung" ("Institute for Nuclear Waste Disposal"), Karlsruhe Institute of Technology (INE-KIT). The intercomparison was done with respect to different redox determination methods, based on static electrodes (platinum, gold glassy carbon, single/combined electrodes), dynamic electrochemical measurements, amperometric measurements, optodes (optical fibres with oxygen sensitive tips) and thermodynamic calculations based on chemical composition and physicochemical properties (such as pH, ionic strength and temperature). For this purpose, a set of samples was used with three different types of origin and properties, namely (i) simple samples with well defined composition, (ii) natural samples to the extent possible kept under near-natural conditions, and (iii) samples with microbial cultures.

The report is based on individual contributions from the ICE participants, summary table with the measured data, discussions and first assessment at the very end of the ICE, minutes of the ICE, discussions during the 2nd Annual Project Workshop, as well as review and discussions following the first draft established in July 2010 and completed during the ICE discussion meeting held in Karlsruhe in October 2010. All participants in the exercise have taken part in the different steps leading to this final report. The report thus reflects consensus between those who have contributed practically and brought in their broad experience.

As main outcome of the exercise, a list of recommendations regarding improved redox measurements was commonly agreed by all the participants and is provided in Section 7 of this report. These recommendations have also led to the identification of future research activities aiming at the improvement of accuracy, reliability and robustness of redox measurements.

A CD-ROM version of the report is available, including the complete set of measured data provided in Excel files, as well as reports from individual groups reflecting own measurements or focussing on the evaluation of sub-systems. The full report can be downloaded free of charge at http://digbib.ubka.uni-karlsruhe.de/volltexte/1000021898 and www.recosy.eu.

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1. Objectives and Key Features

The objectives of the Intercomparison Exercise (ICE) were to compare different redox determination methods in order to (i) identify critical redox determination issues, (ii) provide the basis for more confidence in redox determinations for the individual groups, and (iii) identify future activities that could contribute to further progress in the confidence in determination of the redox state of nuclear waste disposal Safety Case relevant systems and conditions. It is a key element in ReCosy, tackling the central question of how the redox state can be determined, what different redox determination methods register and if differences in the protocols between different groups/organizations are the reason for considerable differences in results reported by different groups.

It is not a prime objective to provide the best estimates for the redox state of the samples used. It is also not the objective to provide a recommended protocol for redox determination. It is recognized, that a recommendation for a redox determination protocol would require an in-depth investigation on the basic processes taking place with different redox determination methods, especially surface processes on electrode material.

The key features of the ICE are:

i. A large number of organizations got together and measured the redox state on a set of samples under well defined conditions. The conditions include that preparing, handling, storing the samples and conducting the investigations/measurements were done in inert gas boxes.

ii. Three different principle approaches were used, namely electrochemical measurements, thermodynamic evaluation of chemical and physico-chemical data, and luminescence measurements using optodes.

iii. The reference and (near-)natural samples were prepared and stored under inert-gas. Two natural samples have been conditioned since more than 15 years, in sealed vessels under inert gas in a fridge. The microbial samples were prepared by MICANS, sent to the host, and stored and treated under inert gas.

iv. Where organizations have immobile equipment, samples were sent to them by the host.

v. The outcome is documented in the present report, communicated, disseminated and brought forward for future development.

2. Samples

Reflecting different purposes, the samples can be divided into the following three types/groups:

1. Well defined reference systems expected to have stable redox conditions. They are of major importance for evaluating the different techniques and handling protocols, and for assessing the correctness of the redox reading. They also cover different pH conditions and include:
   - Fe-system at low ionic strength.

- Fe-system at high salinity/brine conditions.
- System with "simple" organics (e.g. Hydroquinone).
- System under hyperalkaline conditions.

2. A set of near-natural groundwater samples with varying redox stability. Samples include:
    - Groundwater with humic substances (Gorleben, Germany).
    - Clay-rock system (COX, France).
    - Granitic groundwater (Äspö, Sweden; Grimsel, Switzerland).
    - High salinity brines (Asse and Gorleben, Germany).
3. Homogenous systems with microbiological activity.

The samples under points 1 and 2 were prepared by the hosting organization and made available to the partners. As mentioned above, the microbial samples were prepared by MICANS, sent to the host and made available to the participants. The preparation of the iron-mineral suspensions was done with help by Regina Kirsch (FZD) and the hyperalkaline samples were prepared with help from Jan Tits (PSI).

A detailed list of the different samples is given in Appendix I.

3. Participation and structure of the exercise

There were 19 organizations participating in the exercise. Out of these organizations, 15 participated on-site by direct measurements on the samples during the exercise. One of the organizations taking part in the on-site exercise also had samples transferred to their own institute for measurements (ITU). Three organizations (ARMINES, CTH and IPL) did not take part in the on-site exercise, but had samples sent to them for analysis in their home-institutions. One organization contributed by preparing and sending the microbial samples. An overview of the participation is shown in Appendix II.

Each contribution is summarized by a "Individual report". These reports were written by the individual groups taking part in ICE and are included in the CD-ROM complementing this report. A list of all individual reports is provided in Appendix III. A statistical analysis of the data generated during the ICE was conducted by Loughborough University and has been also included in the section "Individual reports" of the CD-ROM.

The approach followed during the exercise was to reserve most of the time for the laboratory studies, with start-up discussion at the beginning of the ICE, and a block of several hours for final discussions in the forenoon of the last day. During this final discussion, a preliminary assessment of the outcome was made, further steps and the time-schedule were agreed upon, and initial conclusions were drawn.

The agreed upon follow-up consisted of the following steps:

i. Participating organizations/groups provide standardized summary outcome reports.

ii. The overall outcome of the ICE is documented in the form of a report (the present document).

iii. The report contains recommendations on possible future activities.

4. Key processes and questions

There are several processes that can have an influence on the determination of the redox conditions of a system. These processes will depend on the determination system. In most cases the determination is made with static electrodes. The primary observation is that the reading obtained with such electrochemical electrode systems frequently does not lead to a stable reading within reasonable time. This may have different reasons that either mean that the "correct value" is slowly approached, or that artefacts lead the system away from a "correct value", or a combination thereof.

In the below discussion, deviation of values from each other is frequently discussed. This should not automatically be understood as a support for several readings clustering around a value as representing "the correct redox state". In order to judge about the correct redox condition, a much more detailed redox determination process understanding is required, well beyond what was identified during drafting and negotiation of ReCosy.

Electrochemical processes on the surface of different noble electrode materials provide the reading of the redox conditions. Pt, but also Au and Glassy carbon are used for this purpose. The redox determination thus depends on the presence, properties of, and processes on these surfaces. Furthermore, a reference system is required introducing further possibilities for different artefacts. The systems measured may also change with time, either through redox processes induced as a pre-requisite for the measurement, or other processes induced by the catalytically active surfaces of the redox electrodes. There may also be degassing or other processes taking place in the system resulting in a change of pH. The redox condition is coupled with the pH and thus this can be an additional reason for drift in the redox determination. Processes and associated questions to be kept in mind when planning, structuring and assessing an intercomparison exercise on redox determination are, amongst other:

i. State of the electrode surface, including the possible impact of pre-treatment protocols,
ii. Time function of adaption to the studied system, as well as possible deviations in the function with progressive chemical poisoning,
iii. Drift in reading through change in electrode surface properties via sorption of material from the studied system, especially solid phases, colloids and polynuclear species,
iv. Catalytic processes taking place on the active electrode surfaces and their impact on the restricted redox buffer capacity of the studied system,
v. Drift in the redox state of the studied system through decompression and degassing, also coupled with drift in pH,
vi. Absolute deviation in reading through diffusion processes over the diaphragm to the reference system, especially where the overall ionic composition/concentration of the solution in the reference system is different than that of the system studied, including diminishing of the absolute deviation through exchange between measured and reference solutions,
vii. Change in reference system potential through exchange of solution with the measured system,

viii. Oxidation of the systems through the non-negligible oxygen content in the inert-gas boxes, or reduction through lower partial oxygen pressure in the inert-gas box atmosphere than the corresponding redox of the solution (only in the case of an equilibrated reaction),

ix. Electrode memory effects: The history of the electrode (previous measurements) may importantly affect the Eh measurements. This information may be relevant in the interpretation of some of the measurements discussed below, and

x. Other processes that have not been identified and documented in this list.

In the ideal case, the ICE measurements will allow identification of relevant processes, and exclusion of non-relevant ones.

5. Outcome

The outcome of the ICE is discussed in different steps. First the preliminary assessment during the last day of the ICE is addressed. Thereafter, the results from the measurements are discussed for the different groups of samples. In addition, the performance of the non-conventional experimental approaches are summarised and compared to the conventional potentiometric techniques used within ICE. Finally, the overall outcome is discussed.

All data measured during ICE is compiled in several Excel files according to the main sample characteristics and distributed on CD-ROM together with this report. Based upon the information given by the ReCosy ICE partners, the raw data, timely response, pre-treatment steps, handling protocols and so forth are summarised for each reference sample. For each of the samples, the measured potential is plotted versus the time of measurement and allows a first evaluation of different techniques and handling protocols.

The data analysis is done in view of different questions. Key questions are:

i. Which measurements show comparable outcome?

ii. What could be the reason for obvious deviations by some measurements?

iii. Which types of time functions are found and at which time intervals?

iv. How does this influence the outcome for a group given the task of determining the redox state of this solution, especially will it end up with a plausible value?

With respect to the last point, it is important to realize, that the present exercise does not allow for unambiguous determination of a “correct value”. It is, however, worth to mention a value resulting from a cluster of a large number of different measurements.

With respect to the third point, one may approach the question of time functions by looking at it both as a linear function with time and as a logarithmic function. This may allow identification of the time function for the analytical system to adapt to the specific redox conditions of the sample. Where such a time function starts will depend on the pre-treatment, including the redox conditions where the system was used prior to the present measurement. In other words, if an electrode surface has been exposed to a more oxidizing environment than that of the measured solution, the value reading should change exponentially from a higher reading, toward a more or less stable reading. The corresponding time function towards a more positive value is expected if the electrode material has been exposed to more reducing conditions prior to measurement. The precondition of the electrode material may be the result of cleaning solutions used during pre-treatment of the electrodes, measurement of a redox buffer, measurement of a previous sample, but also mechanical electrode pre-treatment.

After this adjustment of the electrode surface to the conditions of the specific measurement, a slower, especially linear drift may be observed. Such drift may be the result of changes of the solution redox conditions through air contamination, diffusive change of reference electrode solution and different chemical reactions in the solution, including the catalytic impact from the redox active electrode materials. In those cases the drift should be seen as artefact. It could also be possible, that the electrode system needs a longer time for adjustment to the specific conditions of the measured system.

5.1. Preliminary assessment at the last day of the ICE

A very preliminary assessment on few selected samples was done on the last day of the ICE. For this purpose, the outcome of different measurements was compared on some selected samples subject to multiple measurements. The outcome of this preliminary assessment is given in Appendix IV.

It became obvious that the results from different measurements were not consistent from this short glance at the data. A more detailed assessment was considered necessary as all individual reports had been delivered and the different results could be compared within a broader context.

There were two general questions formulated for the general discussion around the preliminary assessment during the last day of the ICE.

a. Do you feel confident that you can determine the redox state of a system correctly?

b. Can we identify preliminary conclusions on any topics?

With respect to the first question, there was general agreement that the redox state can be determined, however, with a rather low level of confidence.

With respect to the second question, there was some agreement on the following points:

i. There is a slow conversion of the surfaces of the active electrode materials, leading to the partially very long drift observed. A follow-up study should be considered analyzing this conversion of the active surfaces along with drift and equilibration.

ii. Stirring the samples during measurement can decrease the stabilization time.

iii. pH should be monitored simultaneously with the Eh. One concern may be that redox probes are sensitive to local pH variations in their immediate vicinity and that such variations are not correctly represented by measurements with a classic pH electrode in the bulk solution.

The more detailed assessment required is given in the rest of this section 5.

5.2. Dilute Fe systems (REF 1)

The first set of reference samples are iron containing at low salinity (see Appendix I).

5.2.1. REF 1 Fe a

This first Fe containing low salinity sample was prepared without pH buffering. The measuring time reaches up to about 120 minutes. The different measurements do not converge towards a common value. With few exceptions, the individual measurements show a slow logarithmic drift. Exceptions are, especially, BRGM measurements with Au and Pt disk. They seem to show a rapid drift up to some few minutes, followed by continued but slower exponential drift. Beyond some 100 minutes, three different measurements from BRGM move towards a value of about -110 mV. These electrodes are based on Au, Glassy carbon (CG) and Pt disk. The simultaneous BRGM measurement with a conventional Pt electrode, however, drifts towards a value of about 50 mV, coinciding with the value obtained from MSU/INE with a Pt electrode cleaned in water. The other three measurements from MSU/INE (Pt electrode pre-treated by HCl, polished with SiO_2 or pre-treated in the sequence alcohol/silica/HCl) drift towards some 200 mV.

Remaining measurements either do not converge towards a stable value, even after up to 130 minutes measurement, or show comparably stable readings at some -450 mV (PSI) as well as +400 mV (ITU combined Pt electrode under sample stirring). This strong shift, drift and deviations between different methods may indicate that this sample is instable. One potentially important problem with the assessment is this non-buffered sample was that pH was not monitored simultaneously.

5.2.2. REF 1 Fe b

This Fe powder containing pH-buffered sample is systematically measured up to some 30 minutes, with few measurements reaching more than 160 minutes. Most of the measurements show more or less instantly redox potentials around -50 mV. After some 25-30 minutes, the values cluster around some -60 mV. This is also the case for the BRGM measurement with pyrite electrode. Verification measurements by PSI after some 90 minutes, and BRGM with Pt, Au and CG electrodes after more than 160 minutes, verify the values after 25-30 minutes. There are however, also deviating values. IPL has two measurements, where one of them falls in the “bulk range”, whereas the other one shows highly oxidizing conditions (relatively constant at around +350 mV). Very reducing values (-300 to -350 mV) are reported by Amphos and FZD in suspension, as well as potentiometric and amperometric data determined by CNRS.

Compared to the first Fe reference sample, the present pH buffered one shows less scatter and a limited number of values well beyond the majority range. As the pH value has not been determined independently for measurements of the first Fe reference system, it is not possible to judge the pH coupled drift in pe.

5.2.3. REF 1 (II/III) a

This Fe (II) and Fe(III) 1:1 dissolved chloride mixture, MES buffered around pH 5-6, is systematically measured up to about 40 minutes. The results are not very consistent. In general, values of around 300 to 400 mV are determined at around 40 minutes. In logarithmic scale, however, it is shown that also after 4 minutes there is systematic drift, partly “stronger” that in the early part of the measurements. It is therefore not possible to indicate a generally found value after end of major drift.

The considerable differences between single and combined Pt electrode of C. Walther may indicate that not only the material, but also pre-status of the material surface plays a significant role. ITU measurements with oxidized Pt electrodes start at high Eh values with a drift towards lower values. The drift is stronger for the stirred sample, also possibly indicating that the pre-conditioned surface has a substantial influence on the measured value, and that modification of the surface takes more time than the 3/4 h for the present measurements. The stirred sample with the Au combined electrode shows a slow drift from comparably low values, but remains outside the main part of data and timely evolvement. Additional measurements will be required in order to get an insight into the reasons for substantial deviations between measurements of this very oxidized sample. Besides the comparison among differential techniques, thermodynamic calculations of the Eh have been performed by Amphos, BRGM and PSI groups (see individual reports). For samples REF 1 (II/III) a and c, these calculations can be considered accurate enough (concentrations of Fe(II) and Fe(III) in solution high enough). Therefore, a significantly improved level of understanding can be obtained by the use of "reference values" provided by thermodynamics.

5.2.4. REF 1 (II/III) c

This Fe (II) and Fe(III) dissolved chloride mixture was prepared with a Fe(II):Fe(III) ratio of 1:4. The pH of the sample is fixed to 2 with HCl. Many measurements are conducted up to almost 50 minutes. With exception for the CNRS potentiometric measurement, all measurements show convergence towards around +700 mV. Logarithmic scale for the contact/measurement time, however, shows that BRGM Pt, BRGM Glassy carbon and BRGM pyrite rather end the reading drift around some 600 mV. The same value is found for FZD solution measurement. Interesting is that the BRGM measurements with Au and PT disc cluster with the majority of data around 700 mV. The reason for some measurements falling around 100 mV lower than the well converging bulk is not yet understood.

5.2.5. Suspension of Magnetite a and b

These suspended magnetite samples in 0.1 M NaCl at pH 6 and 8, respectively, show consistent values after about 10 minutes measurement time. The respective clusters of values are between 50 and 100 mV for sample "a" (pH 6) and about -250 mV for sample "b". There are some measurements of sample "a" that were interrupted before having reached stable readings. These were measurements from PSI and three ones from ITU. Lin-Log-Extrapolation shows that these measurements should have reached the range of values from the other measurements after about 20 minutes. A very different value is obtained by CNRS (amperometric), whereas the the potentiometric value is in the range of values by other participants.

In summary, the solutions show stable readings. In order to reach stable readings, about 20 minutes is required for some detection systems. The present and also other amperometric measurements show readings significantly different than the bulk number of results from many other methods.

5.2.6. *Suspension of Mackinawite a and b*

These suspended mackinawite samples in 0.1 M NaCl, at pH 6 and 8, respectively, show very different results. The sample “a” at pH 6, shows a great impact of sample treatment. The CNRS amperometric and potentiometric measurements show around -250 mV, together with the measurements PSI and FZD suspension. Contrary to this, the FZD supernatant shows much more oxidizing conditions (around -130 mV) and dramatically more oxidizing conditions for an ultrafiltered sample (slightly above 0 mV). This could indicate that the redox state of the samples strongly depends on the presence or absence of redox buffering solid phase. This could be interpreted in at least two different ways. The first one would be that the sample is subject to permanent oxygen contamination, and that the oxygen is consumed in the suspension but not fully in the supernatant. Another explanation could be that the suspension particles attach to the redox sensor surface creating a local electrochemically active subsystem (also changing its surface properties) and thus affecting the electrochemical reading.

In the sample “b” a very different behaviour is observed. The monitored potentials are deviating from each other for different measurements. Plotting the logarithm of time against the reading, however, it is seen that all measurements are drifting towards the same potential, namely around -300 mV. After some 37 minutes, however, BRGM measurements with pyrite, Au and Pt non-disk electrodes show the occurrence of a disruptive event, the redox potential is increasing abruptly. This may be the impact of oxygen contamination of these samples. Other explanations, however, could also be possible.

In summary, the measurements show the influence of suspended redox buffers, the possible fast response to oxygen contamination both under “normal” inert-gas conditions, and following oxygen contamination, and finally, the potential for suspensions to sorb on electrode surfaces, possibly strongly influencing the electrochemical surface properties and thus the electrode function.

5.3. Brine Fe systems (REF 2)

The second set of references is iron containing samples at high salinity/brine conditions (see Appendix I).

5.3.1. *REF 2 Na a*

This first Fe brine sample is a 5 M NaCl solution with Fe(II)/Fe(III) chlorides, titrated to pH 6-7, the medium without added pH buffer. The BRGM Pt, Au, CG and Pt disk electrodes all drift over the entire measuring time (25 minutes). These samples systematically drift from more oxidizing values and reach about 340 – 370 mV at 25 minutes. The PSI measurement starts with the electrode showing more negative numbers, drifting to more positive ones and after 25 minutes overlap with the above range of the BRGM measurements. The individual values, however continue to drift, and a final stable value is not ensured. The BRGM measurement with pyrite electrode showed complete deviation.

In summary, except for the pyrite electrode, all systems appear to converge towards a relatively narrow value range. However, the values are still drifting after 25 minutes.

5.3.2. REF 2 Na b

This second Fe brine sample is a 5 M NaCl solution with Fe(II)/Fe(III) chlorides, with pH 12 fixed through addition of NaOH. At this pH, a buffer does not appear necessary. Contrary to the pH neutral “a” sample, the present alkaline one shows very deviating potentials. The measurements stop at 24 minutes, with exception for the Amphos one ending after 60 minutes. In all cases, however, the readings are still drifting at the end of measurements. BRGM Au, CG and Pt disk seem to converge towards negative values, at 24 minutes showing between -90 and -140 mV (still drifting). Contrary to this, the BRGM Pt electrode shows a very positive potential, namely around +150 mV after 22 minutes, still drifting towards higher values. The PSI measurement shows potentials around + 100 mV, still drifting towards more positive values after 10 minutes. Amphos readings decrease from around + 155 mV down to about + 60 mV after 60 minutes, still drifting towards lower values. Finally, the BRGM pyrite electrode is used in a time interval from about some 7 to 21 minutes. This measurement shows a value that moves towards the range seen by Amphos.

In summary, the readings drift also after 60 minutes, with different measurements either clustering together or not, and in total ranging from around -150 mV to + 150 mV. An explanation for this wide spread of readings is not yet available.

5.3.3. REF 2 Na c

This third Fe brine sample is a 5 M NaCl solution with Fe(II)/Fe(III) chlorides, with pH 2 fixed through addition of HCl. At this pH, a buffer does not appear necessary. This Fe(II)/Fe(III) containing acidic brine samples show very consistent potentials. The measurements end after around 30 minutes. Extrapolation shows that after 60 minutes, all but one measurement cluster around about 680 mV. The exception is a Pt measurement by BRGM, the same system that has generated values strongly deviating from the bulk of other determinations also in above described systems.

In summary, determination of the redox state of Fe(II)/Fe(III) containing brines under acidic conditions seems to be possible by different methods with a very high degree of confidence. The one strong deviation, however, shows that gravely different readings can be found if relying on only one determination method.

5.3.4. REF 2 Mg b

This Fe(II)/Fe(III) 4.5 M $MgCl_2$ brine sample has a pH of 9, buffered by $Mg(OH)_2(s)$. Measurements are conducted up to about 25 minutes. The measurements show widely different readings and the systems are still drifting after 25 minutes. There is no systematic trend visible between the different readings and the different systems drift towards more positive or more negative values with different intensity.

In summary, the measurements do not allow conclusions concerning a plausible redox value, nor identification of trends.

5.3.5. REF 2 Mg c

This second Fe(II)/Fe(III) chloride 4.5 M $MgCl_2$ brine sample has a pH_c of 2, fixed with HCl. Measurements are conducted up to about 23 minutes, in most cases ending at around 17 minutes. The measurements show readings very similar to that of the acidic NaCl brine (above, REF 2 Na c). The readings cluster at some 680 mV. The BRGM Pt measurement again shows much lower value and is still drifting to even lower readings after 17 minutes.

The conclusion is the same as for the corresponding acidic NaCl brine (see section 5.3.3).

5.3.6. REF 2 Ca b

This Fe(II)/Fe(III) chloride 2 M $CaCl_2$ brine sample has a pH of 12, fixed with $Ca(OH)_2$. Measurements are conducted up to almost 120 minutes, in most cases ending at around 20-22 minutes. The overall observation is comparable to that of the $MgCl_2$ brines at high pH, namely that different measurements show very different values, including drifts without obvious systematic trend. A predictive measurement does not seem possible, different values drifting from less than -150 mV up to just above + 150 mV.

5.3.7. REF 2 Ca c

This second Fe(II)/Fe(III) chloride 2 M $CaCl_2$ brine sample has a pH of 2, fixed with HCl. Measurements are conducted up to just above 20 minutes, in most cases ending at around 17 minutes. The measurements show readings very similar to that of the acidic NaCl brine (above, REF 2 Na c). The readings cluster at some 680 mV. The BRGM Pt measurement again shows much lower value and is still drifting to even lower readings after 17 minutes.

The conclusion is to some extent the same as for the corresponding acidic NaCl brine (see section 5.3.3) and $MgCl_2$ brine (see 5.3.5).

It should be mentioned that a systematic deviation of the measured potential is resulting from a liquid junction potential at the diaphragm of combination electrodes using a standard (3M KCl) junction electrolyte. This effect is studied and reported by GRS within the ReCosy project. The large uncertainties and deviations observed between the different groups however, cannot be explained by this effect.

5.4. Quinone systems (REF 3)

The third set of references is quinone containing samples at low ionic strength (see Appendix I).

5.4.1. REF 3 HS a

The first Ref 3 sample contains hydroquinone at pH fixed to 5-6 with MES buffer. Plotting the data on a linear scale shows a cluster of data up to some 18 minutes contact time with readings around some 270 to 310 mV. This is a relatively small range of variation in the readings. The problem is that there are two additional series of measurements up to almost 110 minutes contact time. These two from IPL and PSI tend towards some 300 mV (IPL) and some 190 mV (PSI). Plotting all the data on a logarithmic scale one could be tempted to conclude that all measurements could meet at around 200 mV at about 1000 minutes. This, however, is a very venturesome, and is probably not reflected in the trends of the IPL data up to some 110 minutes, and is not reflecting the variation in the ITU Pt stirred electrode measurement.

The outcome of an isolated measurement would most probably end with a value around 270 to 310 mV, however also a reading of 170 mV could happen. A reason for the differences between different measurements with this pH buffered sample with 1 mmol/L hydroquinone cannot be given. The range of readings, however, is not excessively large.

5.4.2. REF 3 ISe a

The second Ref 3 sample contains hydroquinone at pH fixed to 8-9 with TRIS buffer, and additionally NaI and $NaIO_3$. A group of measurements result in readings between about 115 and 160 mV. This is not a very large range of scatter. The problem is that the IPL 1st and 2nd measurements give some 170 mV in one case, and a persistent reading over a long time span up to 35 minutes of about 225 mV. Thus, although the sample is well buffered with respect to both pH and Eh, readings vary considerably, in this case by more than 100 mV. In addition, the ITU Pt,ox stirred electrode shows a persistent drop in readings, with about 60 mV at 9 minutes at the end of reading with no sign of stabilized readings.

5.4.3. REF 3 ISe b

The third Ref 3 sample contains Antraquinone and Antrahydroquinone (3:1), reduced by Na-Dithionite, at pH fixed to 5-6 with MES buffer, and additionally 0.1 mmol/L NaI. There are only three measurements of this sample. Two of them are stable with time and show readings between about -70 and -58 mV. A third single reading (FZD) shows a reading of 10 mV after 30 minutes. The sample should be well buffered, both with respect to pH and Eh. Nevertheless, the predictive capability from individual measurements is not very high.

5.5. Hyperalkaline / Cement systems

The fourth set of references consists of hyperalkaline solutions mimicking cement dissolution conditions. The solutions are prepared in a way that strongly reducing conditions are expected (addition of Na-dithionite). The thermodynamics of the redox couple controlling Eh are not well known. Based on the predominance diagram of Chao et al. (1986), above pH=10, Eh values below the water reduction borderline are expected. It is a matter of discussion whether such low Eh values are realistic. Therefore we propose theoretical Eh values in a range between the water reduction border line and the Eh values defined by the $S_2O_4^{2-}/SO_3^{2-}$ redox couple as described by Chao et al. (1986).

5.5.1. REF 4 MQ1

This is a 0.1 mmol/L Ca solution with high (10 mmol/L) Si content. and pH~10.1. The corresponding theoretical Eh range proposed by PSI is in the range of -0.589 V to -0.8V. BRGM Pt and pyrite electrodes show higher readings than the other systems, with the presence of jumps to more positive values. These readings end after some 40 minutes with values of around -400 mV. The readings from University Loughborough show basically stable readings between few minutes and more than two hours, with values closely around -

600 mV. Other readings, mostly ending after 40 minutes, cluster around -650 to -490 mV, spreading over a range of 160 mV.

It is interesting to notice that comparing stirring and not stirring results (PSI) in significantly and systematically lower readings when stirred. For the rest, there are considerable variations in the readings with some values very different from the other ones.

Disregarding the data from BRGM, the agreement among the different experimental Eh values is acceptable. In addition, the agreement of these values with the proposed theoretical Eh value (water reduction border line) is reasonable.

5.5.2. REF 4 MQ2

The difference between this and the above "MQ1" sample is that the Ca concentration is 100 fold higher (10 mmol/L) and the Si concentration is 1000 fold lower (0.01 mmol/L). The pH value of this system is 12.5 and the corresponding theoretical Eh range proposed by PSI is -0.74 V to -1.05 V. The findings are directly comparable with the above ones, with the readings of BRGM Au, GC and Pt stirred, as well as PSI not stirred falling in the range between -700 and -580 mV. The response of the different techniques/electrodes is well comparable with the one found for the "MQ1" sample.

5.5.3. REF 4 ACW1

This sample is directly comparable to the above "MQ1", however, containing 110 mmol/L NaOH and 180 mmol/L KOH, resulting in a pH of 13.3. The corresponding theoretical Eh range proposed by PSI is -0.79 V to -1.1 V. The above mentioned group of detection systems lead to readings after 25 minutes between -750 and -685 mV. This is a relatively narrow range. The measurements of both Amphos and University Loughborough show that the measurement seems to stabilize after some 300 minutes, however, the readings continue to decrease, showing a very slow drift towards even more negative potential after approximately 1000 minutes. The processes leading to this long and slow drift cannot be determined from this measurement. In contrast to the measurements in MQ1 and MQ2, the measurements of Loughborough University in ACW1 do not agree with those obtained by most of the other techniques, showing higher results (ca. -614 mV).

5.5.4. REF 4 ACW2

This sample has the Ca and Si concentrations of the above "MQ2" sample, and the NaOH and KOH concentrations, and pH of "ACW1". The corresponding theoretical Eh range proposed by PSI is -0.79 V to -1.1 V. The conclusions are well comparable to the other hyperalkaline system measurements. One exception is a jump in the reading of University Loughborough that provided values that ranged from -485 mV at the beginning of the experiment, down to -606 mV, after 1000 min.

5.6. (Near)-Natural ground and porewater (NAT)

The fifth set of references corresponds to near-natural, and natural ground- and porewaters (see Appendix I). This group of waters are a challenge both from the viewpoint of representing the real problem, but also because the composition of the water samples is not exactly known. This makes it difficult to relate findings to the underlying chemical processes/reasons. As is also seen, the determination of the redox state is very ambiguous in these samples.

5.6.1. NAT 1a

This is a pH neutral low salinity, high DOC groundwater Gohy-2227, conditioned since 3 July 1991 with the Gorleben Sediment S-102. The groundwater from 128-130 m depth is still available via the corresponding well. The sediment was sampled in frozen condition during construction of the first shaft in the Gorleben underground facility, transported under inert-gas and transferred to an inert-gas box in the lab for further handling.

Several individual measurements appear to reach stability after some 150 to 200 minutes. The problem thereby is that the results of individual measurements deviate very much from each other. After 50 to 100 minutes, where the drift of individual measurements seems to cease, the readings vary from below zero to over 400 mV. In some cases it seems as if there are systematic differences between electrode materials. INE/Huber measurements with single electrodes of Pt drifts towards ~ 250 mV, whereas Au and CG electrodes used simultaneously in the very same samples, and with the same reference, show around 180 mV. Pt electrodes from other groups, however, scatter widely, with “Walther Pt combination electrode” showing results comparable to the INE/Huber ones with Pt single electrode. The Pt single electrode used by Walther, however, shows results rather comparable to the INE/Huber Au and CG electrodes. Another example of the large differences without identification of the reason is comparing the Pt single electrode of INE/Huber with that of Loughborough. The measurements were conducted in the same inert gas-box just opposite of each other. The Loughborough measurement shows a very particular behaviour since the potential reached a steady value at *ca.* +185 mV after only 20 min of continuous measuring, and after 100 min the potential began to decrease steadily, reaching a new plateau at +30 mV after ca 1100 min. This should be compared with the INE/Huber measurement drifting towards some 250 mV. The very low potentials are not only determined by Loughborough, but also by Amphos 1st and 2nd measurements. Interesting enough, the four MSU / INE measurements cluster around 380 mV potential reading, forming an own group of specifically oxidizing results.

Except readings after 1000 minutes and more (up to about 1400 minutes, i.e. basically 24 hours), the measurements from MSU cluster around very positive potential values, ~ 350 mV. Simultaneously, readings from INE/Huber with three electrode materials, shows readings around 160 mV.

There is no systematic reason for the large scatter in readings.

5.6.2. NAT 1b

This is a pH neutral high salinity, low DOC groundwater Gohy-944, conditioned since 2 December 1993 with the Gorleben Sediment S-218. The groundwater from 236-238 m depth is not anymore available as the corresponding well has been removed. The sediment was sampled in frozen condition during construction of the second shaft in the Gorleben underground facility, transported under inert-gas and transferred to an inert-gas box in the lab for further handling.

This brine shows a variation in results very well comparable with the large distribution of readings in the NAT 1a non-brine natural groundwater. As is the case with above, the readings from INE/Huber cluster at one type of values after about 1300 minutes contact time. The University of Loughborough reading stabilizes after some 130 minutes at some +170 mV, not changing much compared to around 1100 and 1200 minutes of contact time. Both cases seen in isolation from each other would lead to the conclusion, that stable reading is achieved. The problem, again, is that the respective values that the different methods drift towards scatter amongst each other (some 380 mV for INE/Huber and about +170 mV for University of Loughborough).

The large differences in the outcome from different methods and organizations shows that predictive calculations based on reliable redox potential readings is not yet possible.

5.6.3. NAT 2

This is a natural Callovo-Oxfordian clay rich rock material, crushed and conditioned with artificial porewater. As is the case with the natural groundwater samples in contact with real sediments, the individual measurements frequently experience diminishing drift in reading until stable values are concluded. As is the case with the two above real groundwater samples, at 100 minutes contact time the readings of individual methods vary between about +100 mV and + 400 mV. Again, the reason for the different readings between the different methods and electrodes is not yet identified.

5.6.4. NAT 3

This is a natural Grimsel crystalline rock material, conditioned with natural Grimsel groundwater. The very low concentrations of potential redox buffer materials indicate the possibility for considerable drift / lack in response of reading.

The results are comparable to the above presented results on natural and near-natural systems. At some 100 minutes contact time, the spread of readings from individual methods stretches from between about -200 to just below + 400 mV. An exception is ITU/Pt with or without stirring, with the reading of about -450 mV coming close to 1000 minutes.

5.6.5. NAT 4

This is a magnesium rich, high salinity brine (IP21 solution), diluted by 10% in order to ensure that over-saturation does not interfere with the measurements. It is an exception under the “real groundwater samples”. After some 200 minutes, the readings of different methods cluster around 650 mV, with no change visible even after about 1700 minutes. There is, however, at least one exception. This exception is University of Loughborough where the readings cluster just below 500 mV already after some 50 minutes, with no sign of changing afterwards.

5.7. Microbial systems (MIC)

The sixth set of references is near-natural, and natural ground- and porewaters (see Appendix I).

5.7.1. MIC A1

The results at a first glance appear to be clear. Looking at measurements up to 120 minutes, five measurements show that the redox potential is around -260 mV. In order to determine this redox potential, the full 120 minutes measurement time is required. There is one exception, namely FZD registering around -140 mV after 30 minutes contact time. The problem with this interpretation is that four out of the five measurements that coincide in their findings are comparable with respect to electrode and pre-treatment. The FZD measurement is not done over time, and thus a trend cannot be deduced. Finally, after 1000 and 1400 minutes contact time, the readings of the four comparably pre-treated electrodes continue to decrease and show about -300 and -315 mV, respectively. An endpoint of this drift is not recognized, and it cannot be said if this drift is relevant or not.

As a conclusion, the measurements indicate a redox potential of about -260 mV, systematically achieved after 120 minutes measuring time. This, however, may be pure coincidence and it is not clear how representative these readings are, and the long-term drift is not understood.

5.7.2. MIC A2, B1 and B2

The number of measurements is too low for any conclusions. A quick glance nevertheless shows that the readings coincide with the findings on sample MIC A1, with respect to method, reading and measurement time.

6. Overall findings

The overall findings are discussed along with the individual groups of samples and overall conclusions.

6.1. Systems

The results are discussed along the different groups of samples.

6.1.1. REF 1 (Low salinity Fe systems)

pH buffered systems with sufficient redox buffer material seem to show consistent readings after some 20 to 30 minutes. Considerable drift in the readings is found when the systems are not stabilized. Despite the partly very consistent results, the predictability based on a single measurement suffers the potential for very different readings. The reasons for such very different readings need to be identified.

6.1.2. REF 2 (Brine Fe systems)

The acidic and pH neutral Fe brine systems show very systematic results with stable readings after some half an hour. Extrapolation indicates that one hour measurement time is preferable. Already at pH of 9, measurements start showing variations and drift without visible reasons. The strongly alkaline samples (pH 12) show variations of ±300 mV without an identifiable reason. Consequently, trustworthy and reasonably precise determination of the redox potential of highly alkaline systems was not possible. In the slightly alkaline range, the $Mg(OH)_2$ buffered system also does not allow determination of the redox potential. To which extent this is the result of chemical, including pH/hydrolysis impact, or if the $Mg(OH)_2$ plays a role for the electrode active surface, cannot be determined.

6.1.3. REF 3 (Quinone systems)

The quinone systems (high concentration of redox active species, and pH buffered) should show rapid convergence towards a small range around one single value. This is confirmed for most measurements. Because of considerable deviations for some measurements, however, the predictive capability from a single redox determination is not satisfactory.

6.1.4. REF 4 (Hyperalkaline systems)

The systems are expected to have very comparable and reducing redox conditions. This is also generally found. Deviations between different redox measurement systems are very systematic between the different solutions. This would indicate that there are very systematic differences between the different electrode materials and geometries, as well as handling (for example stirring or not). The reasons for the different electrode materials to respond as they do, however, are not yet known. Nevertheless, the agreement of the Eh values obtained from most of the methods with the proposed theoretical values is reasonable.

6.1.5. NAT (Natural systems)

The natural samples show large differences between different measurements and sensor systems. There is not yet an explanation available for these large differences. One exception is the Magnesium rich brine. The results underline that there is a problem with reliable prediction of the redox conditions in natural ground- and pore-water systems.

6.1.6. MIC (Microbial systems)

The microbial systems were not subject to a large number of measurements. Interpretation thus is difficult. There is a cluster of readings in the first sample. This cluster, however, represents similar detection systems. The predictive capability thus is limited also from measurements on these microbial systems.

6.2. Non-conventional techniques

A description of the performance of the non-conventional techniques and a comparison with the results from the conventional potentiometric sensors is available at the "Individual reports" folder of the CD-ROM.

6.3. General conclusions

The main conclusion of ReCosy ICE is that the redox state of an aqueous system can be determined by the existing experimental techniques, although the degree of confidence strongly depends of the kind of aqueous system investigated and the degree of optimisation of the experimental equipment and handling protocols. In how far the available experimental accuracy and precision is sufficient to adequately characterise the sample must be assessed in each single case and cannot be generalised.

The overall conclusions from the ICE measurements are that some samples show clusters of readings from different groups and electrodes used. These samples are artificial, with high redox buffer content, with pH buffered and in the pH neutral to acidic range. Highly alkaline artificial samples do not show clustering of the redox readings. Natural samples show very large differences between the different groups, electrodes and handling protocols. A predictive capability based on any of such measurements alone is considered very uncertain. The ICE has not yet provided the basis for identification of different processes responsible for the large drift and large differences in redox readings.

7. Recommendations

Based upon the outcome of ReCosy ICE and the joint data evaluation and interpretation, the partners of ReCosy ICE have agreed on several recommendations. ReCosy ICE was using the presently available experimental and conceptual approaches to compare and evaluate various aspects related to redox measurement and redox data interpretation, aiming at defining the current state-of-the-art. From this concept, two perspectives for generalized recommendations are possible:

(a) Recommendations towards improved quality of redox measurements and data interpretation reflecting the present state of knowledge and methodology.

(b) Recommendations on future research activities that could further improve the reliability of redox measurements beyond what is the current state-of-the-art.

7(a) Recommendations on improved redox measurements

GENERAL ASPECTS

- **It is strongly recommended to use a combination of several experimental approaches to identify and assess systematic errors as there is no single "best method" to determine the redox state of a given system.** This is especially true for the analysis of (intrinsically highly complex) real systems. Ideally, it is recommended to use different sensor materials and complement potentiometric measurements with thermodynamic model calculations based upon the distribution of redox couples.
- The use of a "Quality Assurance" protocol for Eh measurements is advisable. This protocol should consider the use of "validation" solutions, ideally of the same order of magnitude as the sample – both in terms of redox character (oxidizing / reducing) and concentration of redox active species. The check of the reproducibility of Eh readings for unknown samples is an easy but valuable tool in the process of Quality Assurance.
- The use of non-conventional approaches (optodes, amperomentry, …) can help to clarify the redox state and could also be used to complement conventional measurements whenever possible.
- The problems arising from electronics of the instrumentation are generally minor compared to "chemical" interferences affecting redox measurements. In most cases, it is considered sufficient to use commercial equipment (pH-meter, cables, electrodes, ...). The use of amplifiers is recommended only for long (>1m) cables. In all cases, cables should be properly shielded.
- It is recommended to consider that dilution experiments with redox buffers indicate that there is a "critical minimum concentration" of redox active species to allow measurement of meaningful pe values with combined electrodes. In the particular case of dissolved hexacyanoferrate systems at pH 5 and pH 10, this is about 10^{-6} M for individual redox couple components. Similar critical concentrations for Fe have been reported elsewhere (Grenthe et al., 1992).

SAMPLING AND HANDLING

- Transportation of samples can lead to changes in the chemical composition and overall redox state. Measurements should be performed under conditions as close to the real system under investigation as possible, ideally constituting in-situ measurements. Solids present in the system may lead to more stabilized aqueous solutions during storage and transport.
- Redox measurements and sample handling in general should be performed under controlled atmosphere, in most cases meaning inert-gas atmosphere. Ideally, the original atmosphere should be conserved.
- Temperature should be documented for each sampling/measurement, also in regard to the standard potential of reference systems (almost exclusively Ag/AgCl).
- It is useful to explicitly refer to the reference electrode and junction electrolyte used when reporting redox measurements as well as to clearly state whether the reported values have been already converted into Eh (versus SHE). This will significantly reduce uncertainty and puzzling when comparing results from different sources. Bridging / junction solutions should be changed between series of measurements.
- It is recommended to store electrodes under dilute solutions with neutral pH and redox conditions. In the case of combined metal electrodes, the same standard solution as in the bridge (most cases 3M KCl) should be used. The surface of the electrode should be properly “hydrated” prior to use.

EQUILIBRATION / STIRRING

- There is general agreement that stirring samples during measurement leads to the system approaching stable readings more rapidly than without stirring. This is related to the homogenisation of the solution and the decrease of the mass transfer based gradients on active electrode surfaces.
- There is not a full agreement on stirring during reading, mostly because of the difficulties in reproducing the tangential flow velocity caused by stirring when comparing different samples, calibration standards and investigations. It should be noted that online measurements are subject to the same potential difficulties. One may consider performing redox measurements at different tangential flow velocity in order to document a region of limited influence and using this condition for the reading.
- There is no agreement upon the convenience of stirring in the case of heterogeneous samples (presence of solids and/or colloids). The use of protocols considering both stirred and non-stirred measurements could be useful. Whatever the case, it is strongly recommended to document the procedure used.

DRIFT, SURFACE EFFECTS ON SENSOR

- Surface coatings and alterations of the electrode surface are known to influence the performance of the electrode. Cleaning of the electrode surface prior to measurements is recommended, although no agreement on a single optimised pre-treatment protocol has been reached. The use of mechanical polishing, acid cleaner, organic solvents (EtOH) or a combination of all seems to be appropriate under most conditions. The cleaning should focus on the electrode surface, and try to avoid the contact of the diaphragm with the cleaning solution.
- There is a common agreement upon the usefulness of reporting measuring time for each Eh reading, as well as to include a comment on a possible drift in time and the magnitude of this drift. It is strongly recommended to document the criteria used for selecting "correct" readings.
- The "history" of the electrode (previous measurements…) should be known and controlled. The risk of contaminating a sample with traces of other samples, e.g. redox standard solution, should be minimised. This precaution is especially relevant for combined electrodes using a diaphragm into which solution can diffuse easily. It is recommended to use different electrodes for "high concentration" and "low concentration" samples.

pH - pE MEASUREMENTS

- pH measurements should complement redox measurements, as pH conditions and redox potentials are often coupled.
- pH and pe measurements of saline samples give only operational values with no direct thermodynamic significance. These values must be corrected to thermodynamically meaningful values using appropriate correction functions.

THERMODYNAMIC MODELING

- Thermodynamic calculations based upon the concentrations of measured redox couples in solution should be performed with adequate and well documented thermodynamic databases. Information on background ions is required, especially for high saline systems, to allow for proper activity corrections. Specially for high I systems, not covered within NEA-TDB, consistent and reliable ionic strength corrections / activity models are mandatory.
- Thermodynamic calculations based upon the distribution of redox couples are often affected by the experimental limitations in determining redox species, especially when great differences in concentrations occur. It is recommended to critically assess the experimental data prior to calculations, also considering potential kinetic effects on the redox couple equilibration. Calculations based on the analysis of only one redox state, e.g. Fe(II), require data for the solubility limiting solid phases.

*7(**b**) Ideas for future activities from ReCosy ICE*

In addition to the recommendations to improve redox measurements derived from ReCosy ICE, several topics have been identified within ReCosy ICE that may be considered in future research activities related to redox state determination. The main arguments again concern the central question of how the redox state of a system is defined, and what consequences result for redox state determinations? Individual questions related to this overall complex are discussed below.

A) INVESTIGATION OF ELECTRODE SURFACE EFFECTS

- Redox determination with conventional redox electrodes using Pt, Au or Glassy Carbon sensor material is often subject to considerable long-term drift. It would be required to delineate and quantify different reasons for this behaviour in a comprehensive multi-step approach.
- Alteration processes on electrode surfaces will result in “mixed surfaces”, e.g. by sorption of ions, colloids or organics on the sensor material or partial oxidation (e.g. PtO formation) and consecutive surface coating of the sensor. The potential recorded by a “mixed surface electrode” is different from the one measured vs. a clean Pt surface due to mixed potentials being recorded *(mixed potential: the electrode potential of a material while more than one electrochemical reaction is occurring simultaneously)*.
    - The formation of such mixed surfaces should be investigated in more detail, including the critical concentrations for significantly affecting the surface properties.
    - Processes associated with sorption of colloids and sorption of material from suspensions and solid phases should be better understood.
    - The relationship of the formation of “mixed electrode surfaces” with the long-term drift observed during Eh measurements and should be assessed in more detail (see also point E).
- Further systematization and optimization of cleaning protocols for conventional combination electrodes is expected to improve reliability and reproducibility of redox measurements. It is obvious that the factors related to surface coatings mentioned above are influencing redox measurements. Further improved handling protocols are needed to remove surface coatings and ensure clean Pt surface characteristics.
- In many cases, the physical and chemical nature of the chemical gradients inducing the electrochemical surface potential is not well known. Furthermore, it is not known in detail how these gradients are affected by tangential surface flow. It is also not well known how the modifications of these gradients are coupled with the redox bulk conditions. It is thus required to:

  - quantify the physical and chemical gradients of the electrode material surfaces,
  - determine the impact of tangential flow on these gradients, and the corresponding sensor reading, and
  - determine the coupling of these gradients with the bulk redox conditions.

B) IMPROVE FUNDAMENTAL REDOX PROCESS UNDERSTANDING

- It is important to further investigate and systematize which redox couples take active part in establishing the redox state, how they are coupled, which ultimately dominate the total redox state of a system and can thus be used as representative redox indicators. Can recommended analytical protocols or techniques significantly improve investigations based upon analysis of redox couple distributions?
- Empirical observations indicate that “critical minimum concentrations” of redox active components need to be present in solution for redox state determination with combined redox electrodes. How do such critical concentrations depend on the redox couple, on the electrode type or on the system (presence-absence of solid)?
- What are the conditions for active participation of hydrogen and oxygen in the establishing the redox state of systems, as well as determination thereof? How do redox equilibria in the aqueous phase depend on hydrogen or oxygen partial pressure and what are the influences on (mineral) surfaces.
- Better mechanistic understanding and predictability of the role of solids in defining the redox state of a system is needed. Is there a redox gradient between a bulk solution in contact with a solid or solid dispersion, and the direct vicinity of solids or dispersions themselves? If there is such a difference, is this a real redox gradient or is it a consequence of the redox determination method (i.e. interaction of the solid with the electrode – sorption, etc.)?

C) IMPROVE NON-CONVENTIONAL TECHNIQUES

- It has been shown at ReCosy ICE that alternative techniques to complement conventional potentiometric measurements are desired. As none of the non-conventional techniques used in ReCosy ICE at present can be used for routine analysis under reducing conditions, future activities towards an optimization of these approaches are required.
- The feasibility of using “membrane-protected” electrodes to avoid surface alteration effects has been proposed and may be considered for future activities.
- Systematization in the use of in-situ spectrophotometric indicators seems valuable, especially when coupled to comparisons with Eh values obtained by conventional methods for redox determination.

D) ASSESS TEMPERATURE EFFECTS ON REDOX PROCESSES

- At ReCosy ICE attention was entirely focused upon average room temperature conditions. However, many scenarios require predictions under elevated temperature conditions (up to 200°C, depending on repository concept). The redox state of a system will be influenced by temperature and elevated temperature conditions will also affect redox measurements. To account for effects under higher temperatures, it would therefore be necessary to:
    - quantify the impact of temperature on the total redox state of systems, including both aqueous species and solid compounds,
    - assess the influence of more rapid reaction kinetics on the equilibration and distribution of redox couples,
    - quantify the impact of temperature on the experimental determination of the redox state for different measurement approaches,
    - provide a methodology for correcting simple sensor data (such as electrode readings) for determination of the correct redox state, and
    - derive a robust methodology and Thermodynamic Data Base to perform model calculations of redox processes at elevated temperatures, also to countercheck potentiometric data.

E) DEVELOP ADVANCED TOOLS FOR LONG-TIME MONITORING

- In post-closure scenarios, a robust assessment and long-time monitoring (and ideally experimental determination!) of main performance indicators is of high importance. The development of advanced strategies for long-term monitoring of redox conditions is needed. Future research activities could focus on identifying and predicting long-term effects on electrode surfaces, systematizing coating effects and surface alteration processes (closely related to topic A), tailoring long-term stable electrode surfaces and relating the measured potentials to Eh values from conventional Pt sensors.

8. References

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Appendix I: Samples

Sample	Redox-control	Characteristics
REF 1	Fe systems in dilute NaCl (0.1 M NaCl).	
REF 1 Fe a	Fe Powder	~ 100 mg Fe-powder, pH not fixed (~9)
REF 1 Fe b	Fe Powder	~ 100 mg Fe-powder, pH 5-6 fixed with MES buffer
REF 1 (II/III) a	$FeCl_2$, $FeCl_3$	1:1-buffer, 10^{-4} M each, pH 5-6 fixed with MES
REF 1 (II/III) c	$FeCl_2$, $FeCl_3$	1:4-buffer, total Fe is $5x10^{-4}$ M, pH 2 fixed with HCl
REF Sus magn a	Magnetite	Suspension of Fe_3O_4 in 0.1 M NaCl, pH ~ 6 (Prepared by Regina Kirsch)
REF Sus magn b	Magnetite	Suspension of Fe_3O_4 in 0.1 M NaCl, pH ~ 8 (Prepared by Regina Kirsch)
REF Sus mack a	Mackinawite	Suspension of FeS in 0.1 M NaCl, pH ~6 (Prepared by Regina Kirsch)
REF Sus mack b	Mackinawite	Suspension of FeS in 0.1 M NaCl, pH ~8 (Prepared by Regina Kirsch)
REF 2	Brine Fe systems (by adding $FeCl_2$ and $FeCl_3$ stock solutions)	
REF 2 Na a	$FeCl_2$, $FeCl_3$	5 M NaCl, 10^{-4} M Fe(II), Fe(III)-chloride, titrated to pH 6-7 with (HCl, NaOH)
REF 2 Na b	$FeCl_2$, $FeCl_3$	5 M NaCl, 10^{-4} M Fe(II), Fe(III)-chloride each, pH 12 fixed with NaOH.
REF 2 Na c	$FeCl_2$, $FeCl_3$	5 M NaCl, 10^{-4} M Fe(II), Fe(III)-chloride each, pH 2 fixed with HCl.
REF 2 Mg b	$FeCl_2$, $FeCl_3$	4.5 M $MgCl_2$,10^{-4} M Fe(II), Fe(III)-chloride each, pH 9 fixed with $Mg(OH)_2$(s).
REF 2 Mg c	$FeCl_2$, $FeCl_3$	4.5 M $MgCl_2$, 10^{-4} M Fe(II), Fe(III)-chloride each, pH 2 fixed with HCl.
REF 2 Ca b	$FeCl_2$, $FeCl_3$	2 M $CaCl_2$, 10^{-4} M Fe(II), Fe(III)-chloride each, pH 12 fixed with $Ca(OH)_2$(s).
REF 2 Ca c	$FeCl_2$, $FeCl_3$	2 M $CaCl_2$, 10^{-4} M Fe(II), Fe(III)-chloride each, pH 2 fixed with HCl.
REF 3	0.1 M NaCl samples with simple organics.	
REF 3 HC a	Hydroquinone	10^{-3} M Hydroquinone, pH 5-6 fixed with MES buffer
REF 3 ISe a	Hydroquinone	10^{-3} M Hydroquinone, pH 8-9 fixed with TRIS, + 10^{-4} M NaI and $NaIO_3$
REF 3 ISe b	Anthrahydroqu.	Anqui:Anhyqui = 3:1 (total $1.6x10^{-3}$ M) reduced by Na-dith., pH 5-6 fixed with MES, + 10^{-4} M NaI
REF 4	Artificial cement systems under hyperalkaline conditions (pH 10 – 13.3) (Prepared by J. Tits, PSI, Na-dithionite spiked at KIT-INE)	
REF 4 MQ1	Na-dithionite	[Ca] = $1E^{-4}$ M; [Si] = $1E^{-2}$ M [Na] = 0 M; [K] = 0 M
REF 4 MQ2	Na-dithionite	[Ca] = $1E^{-2}$ M; [Si] = $1E^{-5}$ M [Na] = 0 M; [K] = 0 M
REF 4 ACW1	Na-dithionite	[Ca] = $1E^{-4}$ M; [Si] = $1E^{-2}$ M [Na] = 0.11 M; [K] = 0.18 M
REF 4 ACW2	Na-dithionite	[Ca] = $1E^{-2}$ M; [Si] = $1E^{-5}$ M [Na] = 0.11 M; [K] = 0.18 M
NAT	(Near-)natural ground- and porewater	
NAT 1a	-	Gorleben Sediment S-102 with low salinity groundwater Gohy-2227, conditioned since 3 July 1991.
NAT 1b	-	Gorleben Sediment S-218 with brine Gohy-944, conditioned since 2 December 1993.
NAT 2	-	Crushed COX Material equilibrated with artificial COX pore water (Prepared at KIT-INE by Th. Schäfer)
NAT 3	-	Crushed Grimsel material equilibrated with natural Grimsel groundwater (Prepared at KIT-INE by Th. Schäfer)
NAT 4	-	Magnesium rich high salinity brine, (IP21 Solution), 10% dilution factor
MIC	Microbial systems (Prepared by MICANS / K. Pedersen and shipped to KIT-INE)	
MIC A1	-	Sulphate reducing bacteria medium with growing *Desulfovibrio aespoeensis*
MIC A2	-	Sulphate reducing bacteria medium, sterile
MIC B1	-	Autotrophic acetogenic medium with growing *Acetobacterium carbonolicum*
MIC B2	-	Autotrophic acetogenic medium, sterile

Appendix II: Participation

Participant	Organization	Involvement	Samples
Bischofer, Barbara Scharge, Tina	GRS (DE)	Pt electrode and thermodynamic evaluation (Spectroscopy Fe^{2+}/$^{3+}$)	Ref(II/III)(c), Ref2Na(c), Ref2Mg(c), Ref2Ca(c), Nat4
Kumke, Michael Steinbrück, Dörte	UPPC (DE)	Optode measurements	Nat1(a,b), Nat(2,3), Mic(A1,A2,B1)
Oh, Jae Yong	KAIST,AG (KR)	See Riba, Olga	
Perdicakis, Michel Streiff, Carine	CNRS (FR)	Potentiometry (single Pt electrodes) Amperometry (Pt ultramicroelectrodes)	REF1 Fe (a,b), REF1 II/III (a,c), REF1 (sus. Magn. a & Mack. a), REF2 Na (a,b,c), REF3 (HCa, ISe a, ISe b), NAT2 & NAT3.
Tits, Jan Gaona, Javier	PSI (CH)	Combined Electrodes	All except microbial
Wegen, Detlef	ITU (EC)	Combined Electrodes, Controlled area	
Seibert, Alice			
Gouder, Thomas			
Carbol, Paul			
Fellhauer, David		See Kirsch, Regina	
Jain, Sneh Felipe-Sotelo, Monica	ULOUGH (UK)	Self-made single electrodes	Ref2Ca(b). Ref4MQ(1,2), Ref4ACW1,2), Nat1(a,b), Nat2,3,4)
Ignatiadis, Ioannis Betelu, Stéphanie	BRGM (FR)	Au, Pt and C-Glass Electrodes	Ref01Fe(a,b), Ref01(II/III) (a,c), RefSuspensionMackinawite(b), Ref02Na(a,b,c), Ref02Ca(b,c), Ref02Mg(b,c), Ref04MQ(1,2), Ref04ACW(1,2), Nat02
Krawczyk-Bärsch, Evelyn	FZD (DE)	Micro Pt-Combination Electrode	Ref3HC(a), Ref3ISe(a,b), Nat1(a,b), Nat2,3,4, MicA1,2, MicB1,2
Kirsch, Regina	FZD-ROBL (DE)	Pt-Combined Electrode	Ref1Fe(a,b) Ref1(II/III)(a,c), RefSusMag(a,b), RefSusMack(a,b)
Petrov, Vladimir	MSU (RU)	Pt-Combination electrode, different pre-treatments	
Kuczewski, Bernhard	UKOE,AG (DE)	CE-ICPMS (I, Fe?)	Ref1Fe(a,b), Ref(II/III)(a,c), RefHC, RefISe(a,b), Nat1(a,b), Nat(2,3)
Marosits, Edit	TUG (AS)	See Kuczewski, Bernhard	
Marquardt, Christian	KIT-INE (DE)	See Kuczewski, Bernhard	
Huber, Florian Müller, Nikolaus		Different commercial single electrodes	REF1Fe(a), Nat1(a), NAT1(b), NAT3
Walther, Clemens Icker, Mirek		Different Electrodes and different electronic devises	REF1(a), REF1(c), NAT1(a), NAT1(b), NAT3, NAT4
Sasaki, Takayuki	KYU,AG (JP)		

Riba, Olga	AMPHOS (ES)	Pt-Ag/AgCl	Ref1Fe1(a,b), Ref1(II/III)a, RefSusMagn(a,b), RefSusMack(b),Ref2Na(b), Ref2Ca(b), Ref3ISe(b), Ref4ACW(1,2), Nat1(a,b), Nat(2,3,4)
Not participating on-site, but analyzing samples sent to them			
Ekberg, Christian Ödegaard-Jensen, Arvid Allard, Staffan	CTH (SE)	Determination of redox state of chemical elements	Ref1Fe(b), Ref1(II/III)(a), Ref3HCa, Ref3ISe(a), Ref4ACW(1,2), Nat1(a), Nat(2,3)
Lujaniene, Galina	IPL (LT)	Combined Pt electrode	Ref1Fe(b), Ref1(II/III)(a), Ref3HCa, Ref3ISe(a), Ref4ACW(1,2), Nat1(a), Nat(2,3)
Grambow, Bernd	ARMINES(FR)	CE-ICPMS	Ref4MQ(1,2), Ref4ACW(1,2)
Organization and support			
Altmaier, Marcus Buckau, Gunnar Kienzler, Bernhard Schäfer, Thorsten	KIT-INE (DE)	Scientific organization and support	
Bohnert, Elke Müller, Nikolaus		Technical organization and support	
Böttle, Melanie		pH and Eh Pt-Combination Electrode after 15 minutes	
		Chemical analysis of Na, K, Mg, Ca, Cl and SO_4^{2-}	
Pedersen, Karsten	MICANS (SE)	Providing the microbial samples	

Appendix III: List of reports from individual partners

The reports below were prepared by individual groups and are provided separately in the CD-Rom version of this report.

Amphos 21 – KAIST

O. Riba, J. Y. Oh, M. Grivé. „*Redox potential measurements to assess the equilibration times of the electrode*".

BRGM

S. Betelu, C. Tournassat, I. Ignatiadis. „*Redox potential measurements using different electrodes and comparison with equilibrium potential computed by geochemical modelling*"

CNRS

M. Perdicakis, C. Streiff. „*Application of the potentiometric and the amperometric methods for the redox potential determination*"

CTH

S. Allard, C. Ekberg, S. Holgersson, G. Skarnemark, K. Spahiu, A. Ödegaard-Jensen. „*Agreement between measured Eh and quantification of oxidation states*".

FZD – ROBL

- E. Krawczyk-Bärsch. „*Report and evaluation of the redox potential measurements during the Intercomparison Exercise of ReCosy*".
- D. Fellhauer (ITU), R. Kirsch. „*Comparing the impact of measuring in suspension, after centrifugation and after ultra-filtration on the obtained pe and pH values and comparing with pe-values calculated from photo-spectrometrically determined Fe(II) and Fe(III) concentrations*"

GRS

B. Bischofer, T. Scharge, S. Hagemann. „*Redox Measurements of Saline Samples by Spectrophotometric and Potentiometric Methods*".

IPL

G. Lujaniene. „*Individual report by IPL*".

JRC-ITU

D.H. Wegen, A. Seibert, P. Carbol. „*Uncertainties in Redox Potential Measurements Redox measurements carried out at ITU*"

KIT-INE

- F. Huber, N. Müller, G. Buckau. „*Separation of drift on reference and active electrode*"
- M. Icker, C. Walther. „*Separation of drift on reference and active electrode*"
- V. Petrov (MSU), M. Böttle, M. Altmaier. „*Test of cleaning protocols for (Pt) combination electrodes*"

PSI-LES

J. Tits, X. Gaona. „*Measurement of redox potentials in reference solutions with a combined redox electrode. Effect of measurement time. Comparison with thermodynamic calculations*".

TUG – INE – UKOE

B. Kuczewski, M. Lagos, C. M. Marquardt, E. Marosits, C. Dully. „*Determination of redox species of iodine and iron with CE-ICP-MS*"

ULOUG:

- S. L. Jain, M. Felipe-Sotelo. „*ReCosy Intercomparison Exercise Workpackage 2*“.
- M. Felipe-Sotelo. „*ReCosy Intercomparison Exercise: Statistical analysis*“.

UPPC

D. Steinbrück, M. U. Kumke. „*Fiber-optical sensing of oxygen in reference and natural samples*“.

Appendix IV: First on-site evaluation

Sample (pH)	Organization/Group	Eh	Comment
Ref1Fe(a)			
pH 8.5	INE/MB	-392	Pt combination electrode, 15 minutes
	MSU	-280 ± 60	
	AMPHOS/KAIST	-250 (-370)	In Fe suspension (after cleaning the electrode)
pH 8.6 ->	PSI	-460 ± 50	In Fe suspension
	ITU/DF+CNRS/RK	-350 / -75	In suspension / suspension separated
pH 8.0 ->	BRGM	-190	After 15 minutes with Au, Pt and CG
	ITU/??	400	
Ref1(II/III)(a)			
pH 5.3	INE/MB	-12	Pt combination electrode, 15 minutes
	ITU/DF+CNRS/RK	42, 250	First value in suspension, second in supernatant
	PSI	360	Suspension
	INE/CW	300	
	ITU/??	365	
	AMPHOS/KAIST	300	Stable after 4 min.
pH 5.0 ->	BRGM	340	
	CNRS/MP	297, 72	Potentiometric , Amperometric
Ref2C(b)			
pH_c ≈12	INE/MB	-261	Pt combination electrode, 15 minutes
	MSU	18	As above, but stirring
(pH 10 ->)	BRGM	-85	
	ULOUGH	20	Stable after 20 min.
	AMPHOS/KAIST	85	Stable after 2 minutes
	PSI	100	
Ref3HC(a)			
	INE/MB	120	Pt combination electrode, 15 minutes
	FZD	255	
	ITU/DF+CNRS/RK	308	Pt
	ITU/DF+CNRS/RK	311	Au
	PSI	190	
Ref4MQ1			
pH 9.55	INE/MB	-370	Pt combination electrode, 15 minutes
	BRGM	-512	After 10 minutes response, then stable 30 min.
	ULOUGH	-785	
	PSI	-560	
Nat1(a)			
pH 8.6	INE/MB	230	Pt combination electrode, 15 minutes
	MSU	330 ± 40	
	FZD	160	
	ULOUGH	-148	After 24 h (strong drift in beginning)
	INE/CW	210	
	PSI	190	Stable after 15 min stirring
	INE/FH	163	Pt, 16 h
	INE/FH	130	Au, 16 h
	INE/FH	170	CG, 16 h
	AMPHOS/KAIST	28	Very stable from beginning to over 1 h
Nat2			
pH 7.87	INE/MB	120	Pt combination electrode, 15 minutes
	INE/CW	270	
pH 8.38	ULOUGH	81	10 h until stable
	FZD	240	
	AMPHOS/KAIST	100	Strong variations
	PSI	250	Stable after 10 min stirring

	BRGM	260	Stable after 2 h, remains stable 24 h
Nat3			
	INE/MB	224	Pt combination electrode, 15 minutes
	ITU/DF+CNRS/RK	70	Pt
	ITU/DF+CNRS/RK	296	Au
	FZD	156	
	INE/CW	230	
	ULOUGH	12	2 hours contact time
	INE/FH	298	Pt, 17 h, still drifting
	INE/FH	187	Au, 17 h, still drifting
	INE/FH	160	CG, 17 h, still drifting
	PSI	260, 140	Parallel samples, 15 min stirring
	AMPHOS/KAIST	-30	1 h
Nat4			
pH 0.5	INE/MB	408	Pt combination electrode, 15 minutes
	ULOUGH	490	Stable for 20 min.
pH_c 3.0	INE/CW	640	
	GRS/BB	677 (760)	In brackets, corrected for salinity
	GRS/TS	680	Fe-analytics
	FZD	635	After 45 min., still drifting
	PSI	580	
	AMPHOS/KAIST	660	

Appendix V: Information on the potentiometer and electrodes used by the participants

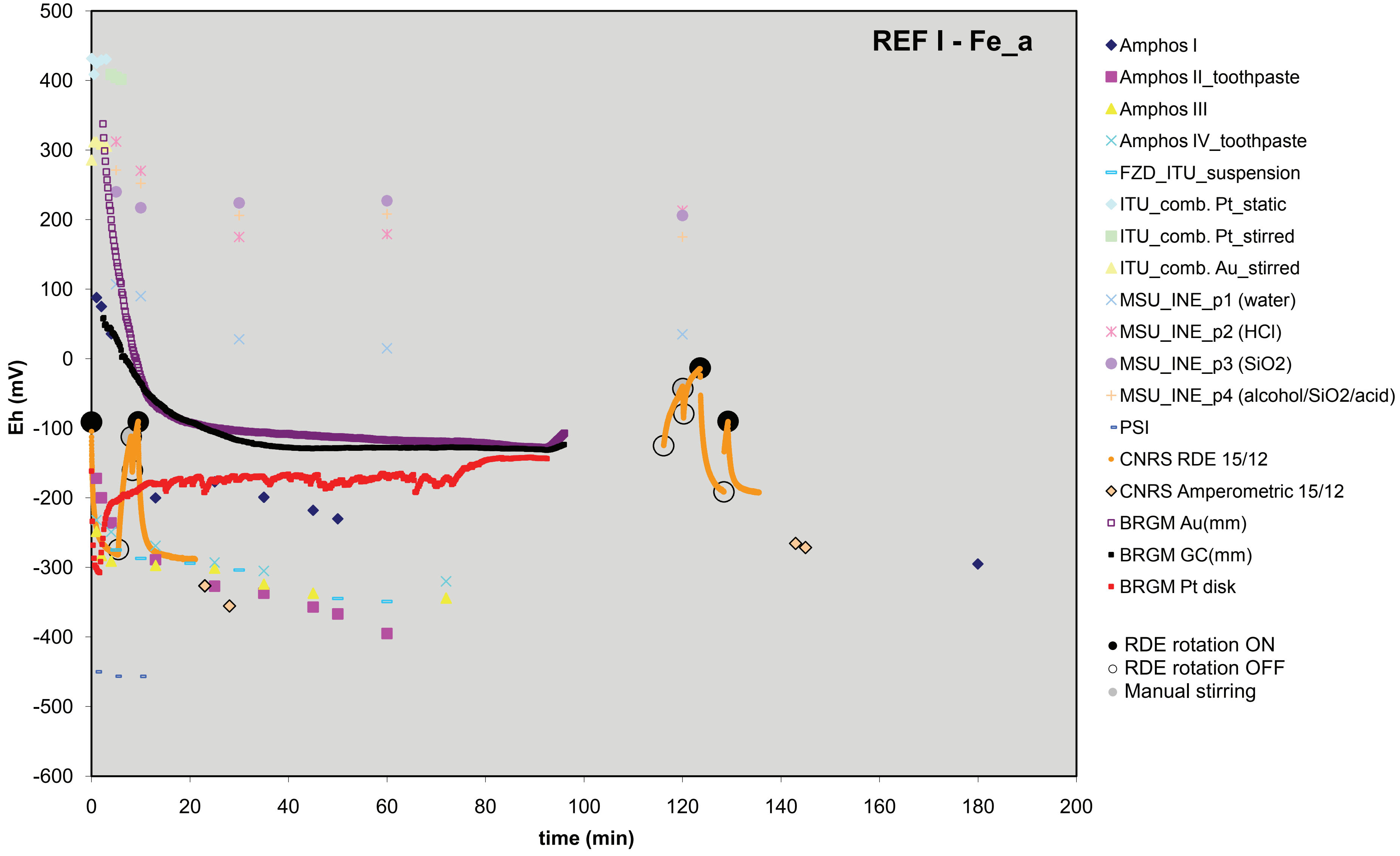
Participant	Potentiometer			Electrodes			Stirring method
	Model	Input impedance	Offset curent	Nature	Model	Surface or size	
AMPHOS	pH 3000 (WTW)	$>5\times10^{12}$ Ω	$<5\times10^{-13}$A	Combined Pt/AgAgCl/3 M KCl	Hamilton Glass ORD		Continuously, magnetic stirrer bar (1cm x 2mm)
BRGM	2700 Multimeter (Keithley)	$>10^{10}$ Ω		Pt disk shaped Au disk shaped GC disk shaped Pyrite cylindrical (Py1) Pyrite cylindrical (Py2)	 homemade homemade	10 mm (78.54mm²) 2 mm (3.14mm²) 2 mm (3.14mm²) 229 mm² 177 mm²	Magnetic stirrer
CTH	pH M 240 (Radiometer)	$>2\times10^{12}$ Ω	$<5\times10^{-13}$A	Combined Pt ring/AgAgCl/3 M KCl	InLab Redox Micro Pt ring (Mettler Toledo)		Occasionally stirred by gently shaking the vessels
CNRS LCPME	Quad Amp pH/mV (eDAQ Pty Ltd)	10^{13} Ω	3×10^{-14} A	PtRDE , ∅ = 2 mm	Tacussel	3.14 mm²	Rotation (If suspension rotation + magnetic stirrer)
				Pt wire, d=1mm h=10mm Pt rod, d=2mm h=30-40mm	Tacussel Metrohm	7.85 mm² 92-125 mm²	Magnetic stirrer
FZD ITU	Orion ?			Combined Pt ring /AgAgCl/3 M KCl	Metrohm		"hand-stirring"+ static measurement
FZD				Single miniaturized Pt	Unisense	tip diameter 10µm	Non stirred
GRS	713 pH-meter,(Metrohm)	$>10^{13}$ Ω	$<3\mathrm{x}10^{-13}$A	Combined Pt/AgAgCl -ring electrode	Metrohm 6.0451.100	~ 60mm^2	"stirred"
INE_Huber				Pt electrode vs AgAgCl/3 M KCl Au electrode vs AgAgCl/3 M KCl GC electrode vs AgAgCl/3 M KCl			20min stirring+5min static, then 1 min. reading/
INE_Walther	Impedance converter (home built vs. comercial) + read-out unit (multimeter vs. Orion)			Combined Pt_ring /AgAgCl/3 M KCl Single Pt wire/AgAgCl micro electr.	Metrohm KSI Meinsberg		Non stirred
MSU INE	Orion ?			Pt_ring/AgAgCl/3 M KCl combined	Metrohm		Static
PSI	780 pH meter (Metrohm)	$>10^{12}$ Ω	$<10^{-12}$A	Combined Pt_ring /AgAgCl/3 M KCl	Metrohm		"stirred"
ULOU	Potentiostat: VersaStat 3 (Princeton Applied Research)	$\geq 10^{12}$Ω	≤ 5pA	Working electrode 1: Pt wire Working electrode 2: Pt mesh	Working electrodes 1 & 2: Inlab Reference: Metrohm	Working electrode 1: 0.5 mm dia. Working electrode 2: 5 mm x 9 mm	Stagnant conditions
ITU	pH/Oxi Oxi 340i (WTW)	$>10^{12}$ Ω		Combined Pt_ring /AgAgCl	SenTix ORP (WTW)	56.5mm^2 (6mm diameter, 3 mm	Variable
				Combined Au_ring /AgAgCl/Gel Au4805-DPA-SC-S8/120	Mettler Toledo	56.5mm^2 (6mm diameter, 3 mm width	
IPL	Inolab Multilevel 1, (WTW)			Combined Pt_ring/AgAgCl combined Au_ring /AgAgCl/Gel	SenTix ORP (WTW) Mettler Toledo		
CHALMERS UNIVERSITY	pHM 240,(Radiometer)			Ag/AgCl (3M KCl) electrode with Pt ring	Mettler Toledo Inlab Redox Micro		"occasionally stirred by gently shaking the vessels"

ISSN 1869-9669

Experimental data – Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems

FP 7 EURATOM Collaborative Project Redox Phenomena Controlling Systems

The complete set of measured data are provided as Excel files in the CD-ROM version of the report, and can be also downloaded free of charge via ReCosy webpage at www.recosy.eu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400
300
200
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-200
-300
-400
-500
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time (min)
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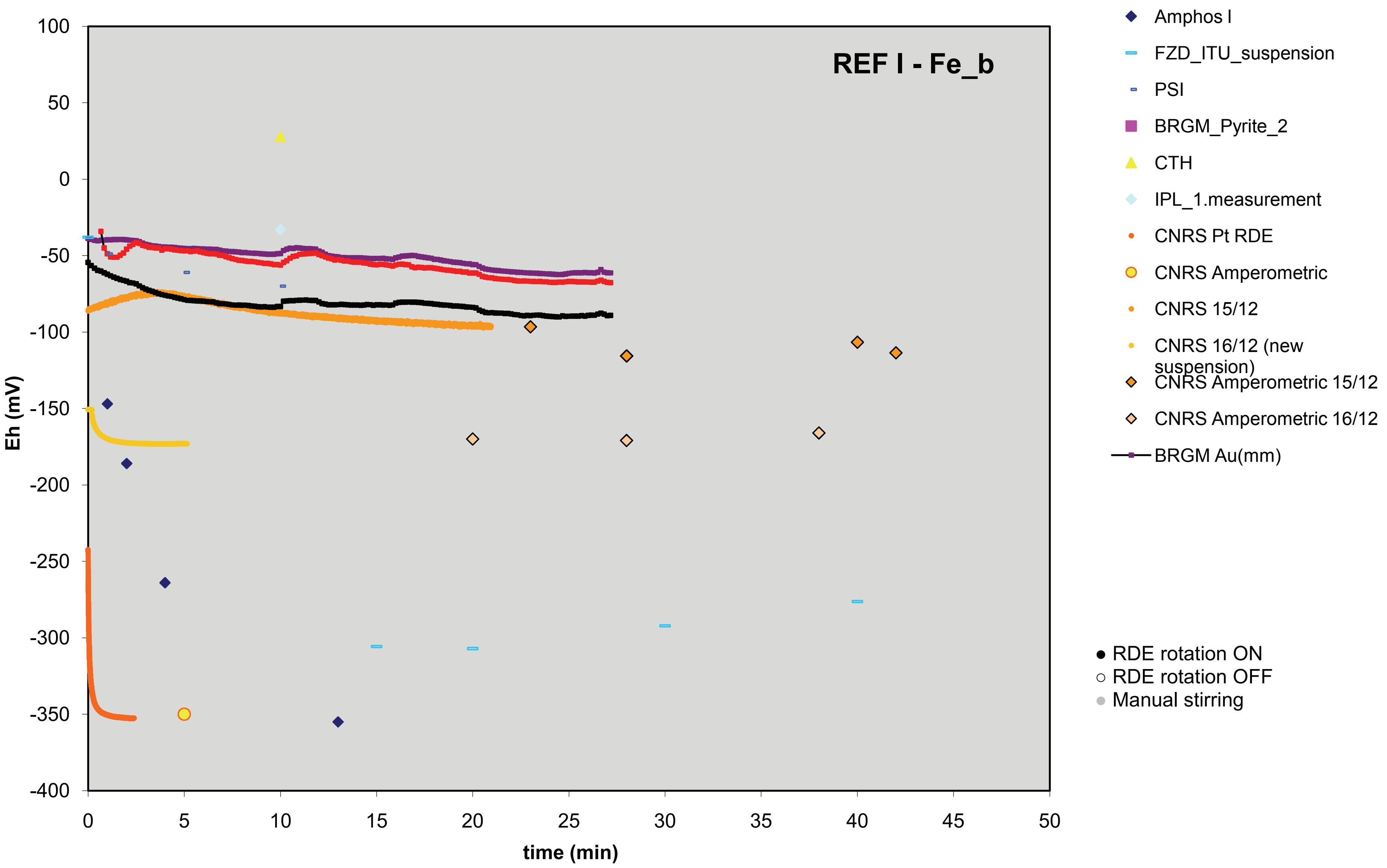
20
40
60
80
100
120
140
160
180
200
Amphos I
Amphos II_toothpaste
Amphos III
Amphos IV_toothpaste
FZD_ITU_suspension
ITU_comb. Pt_static
ITU_comb. Pt_stirred
ITU_comb. Au_stirred
MSU_INE_p1 (water)
MSU_INE_p2 (HCl)
MSU_INE_p3 (SiO2)
MSU_INE_p4 (alcohol/SiO2/acid)
PSI
CNRS RDE 15/12
CNRS Amperometric 15/12
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk
RDE rotation ON
RDE rotation OFF
Manual stirring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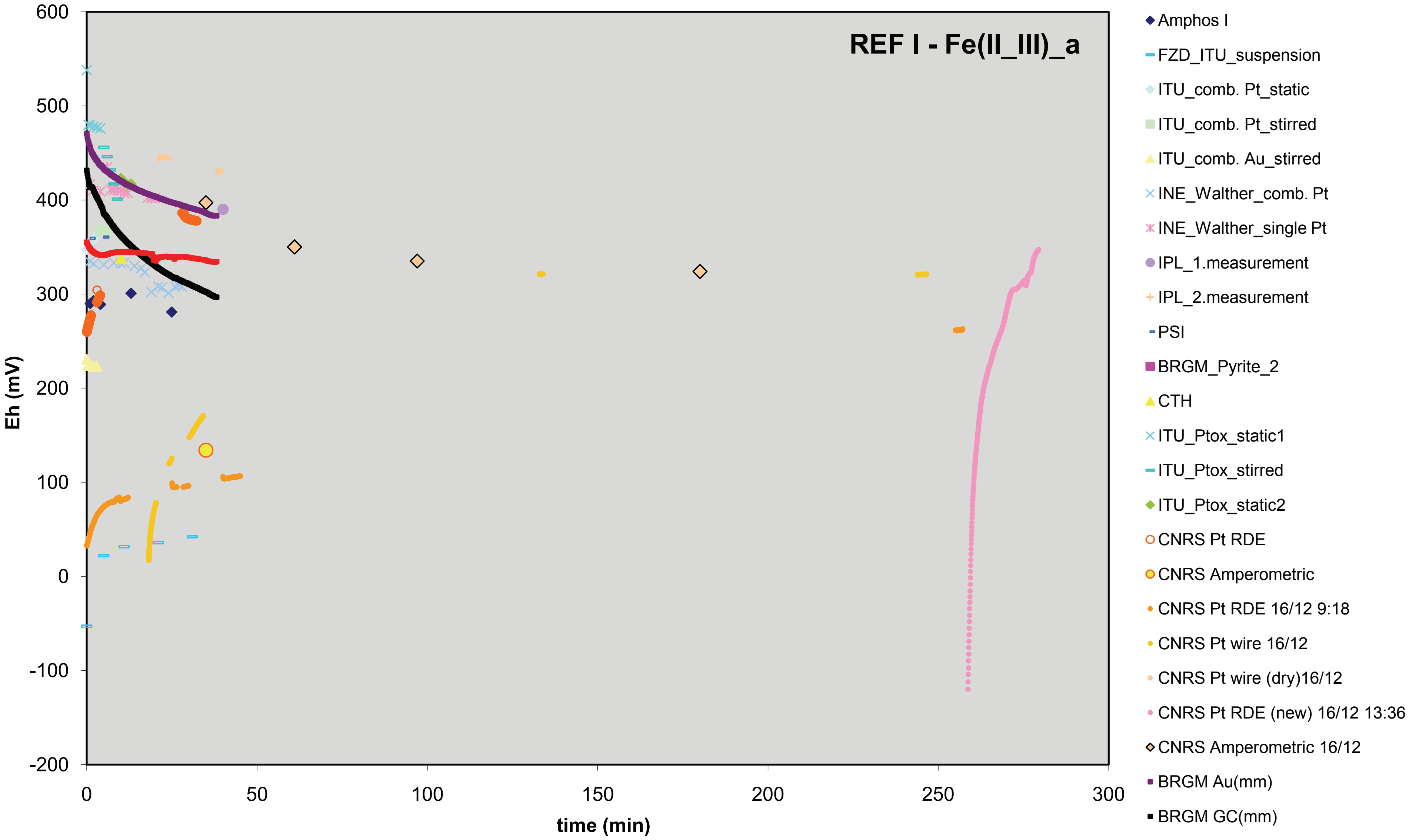
-50
-100
-150
-200
-250
-300
-350
-400
0
5
10
15
20
25
30
35
40
45
50
time (min)
◆ Amphos I
FZD_ITU_suspension
PSI
■ BRGM_Pyrite_2
▲ CTH
◆ IPL_1.measurement
● CNRS Pt RDE
○ CNRS Amperometric
● CNRS 15/12
● CNRS 16/12 (new suspension)
◆ CNRS Amperometric 15/12
◇ CNRS Amperometric 16/12
BRGM Au(mm)
● RDE rotation ON
○ RDE rotation OFF
● Manual stirring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Eh (mV)
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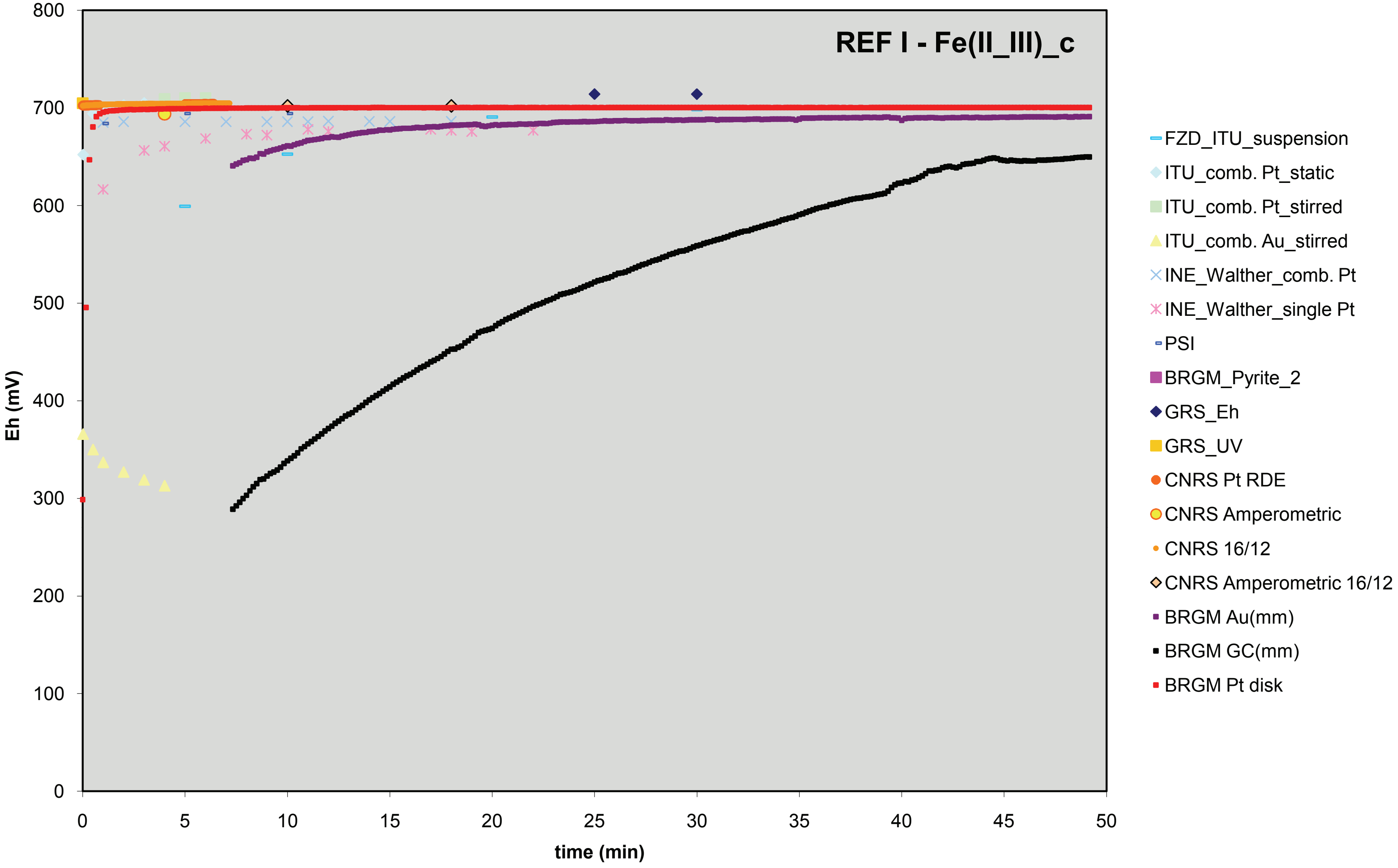
500
400
300
200
100
0
-100
-200
0
50
100
150
200
250
300
time (min)
Amphos I
FZD_ITU_suspension
ITU_comb. Pt_static
ITU_comb. Pt_stirred
ITU_comb. Au_stirred
INE_Walther_comb. Pt
INE_Walther_single Pt
IPL_1.measurement
IPL_2.measurement
PSI
BRGM_Pyrite_2
CTH
ITU_Ptox_static1
ITU_Ptox_stirred
ITU_Ptox_static2
CNRS Pt RDE
CNRS Amperometric
CNRS Pt RDE 16/12 9:18
CNRS Pt wire 16/12
CNRS Pt wire (dry)16/12
CNRS Pt RDE (new) 16/12 13:36
CNRS Amperometric 16/12
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk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Eh (mV)
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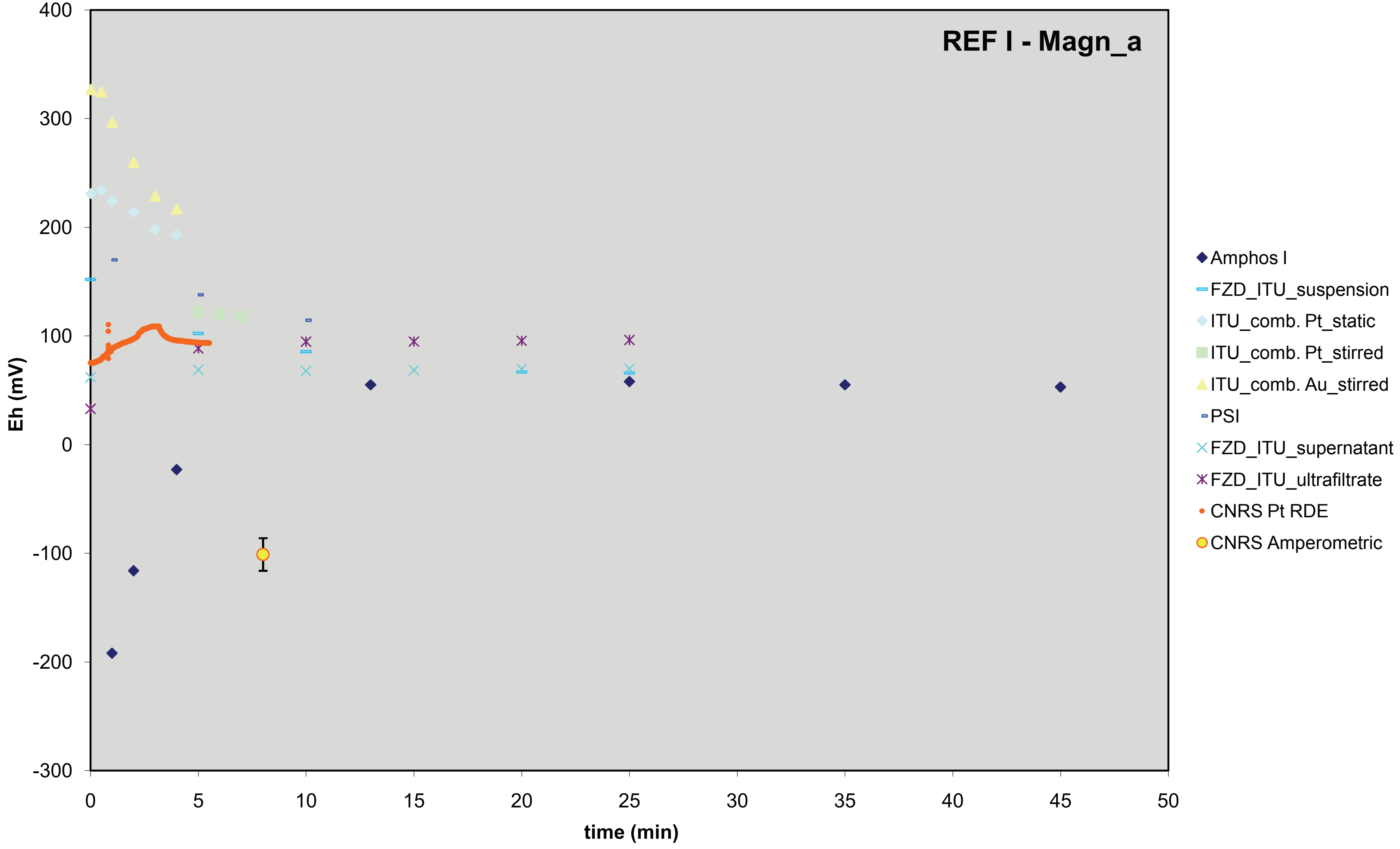
700
600
500
400
300
200
100
0
time (min)
0
5
10
15
20
25
30
35
40
45
50
FZD_ITU_suspension
ITU_comb. Pt_static
ITU_comb. Pt_stirred
ITU_comb. Au_stirred
INE_Walther_comb. Pt
INE_Walther_single Pt
PSI
BRGM_Pyrite_2
GRS_Eh
GRS_UV
CNRS Pt RDE
CNRS Amperometric
CNRS 16/12
CNRS Amperometric 16/12
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk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time (min)
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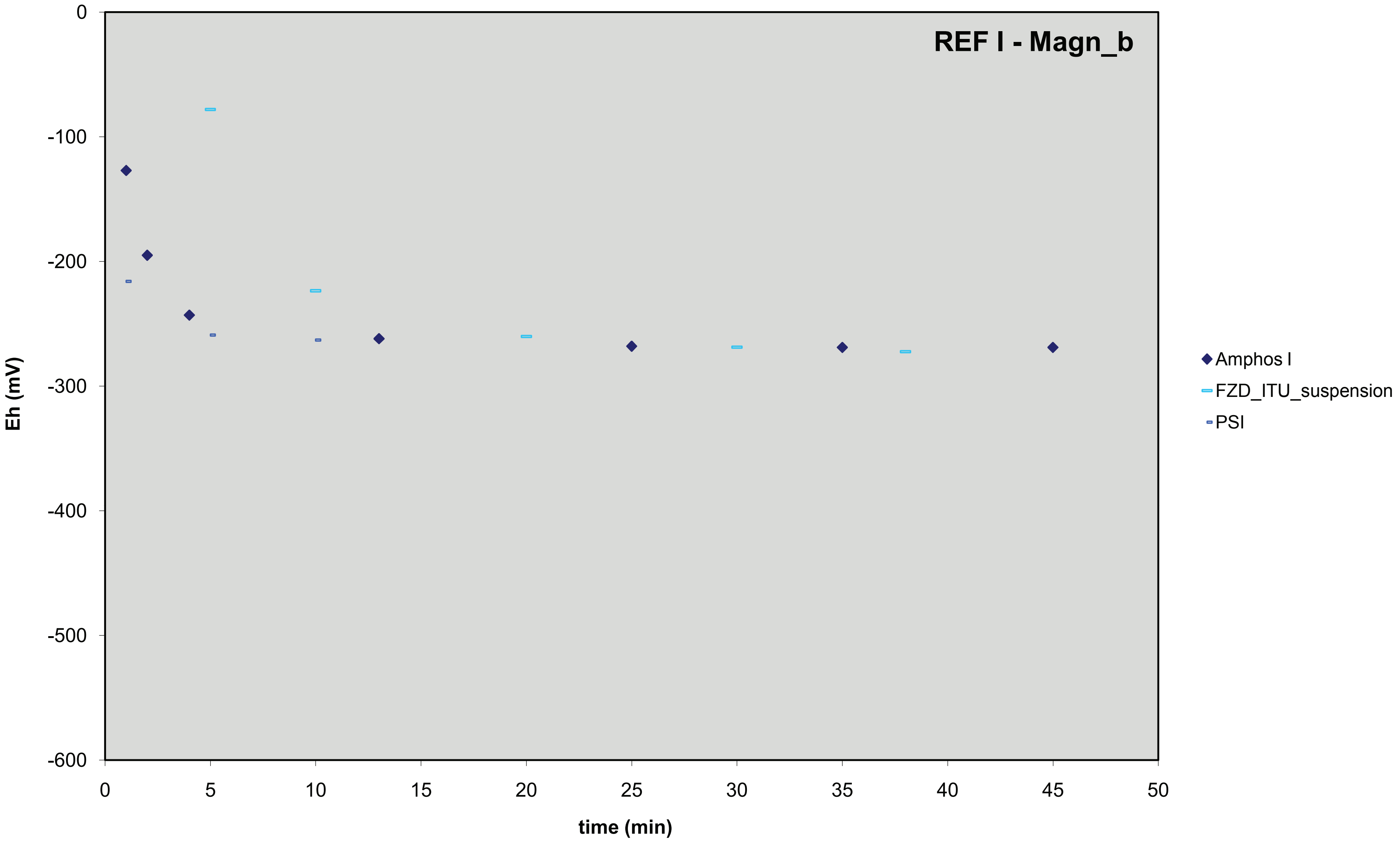
300
200
100
0
-100
-200
-300
0
5
10
15
20
25
30
35
40
45
50
Amphos I
FZD_ITU_suspension
ITU_comb. Pt_static
ITU_comb. Pt_stirred
ITU_comb. Au_stirred
PSI
FZD_ITU_supernatant
FZD_ITU_ultrafiltrate
CNRS Pt RDE
CNRS Amperometric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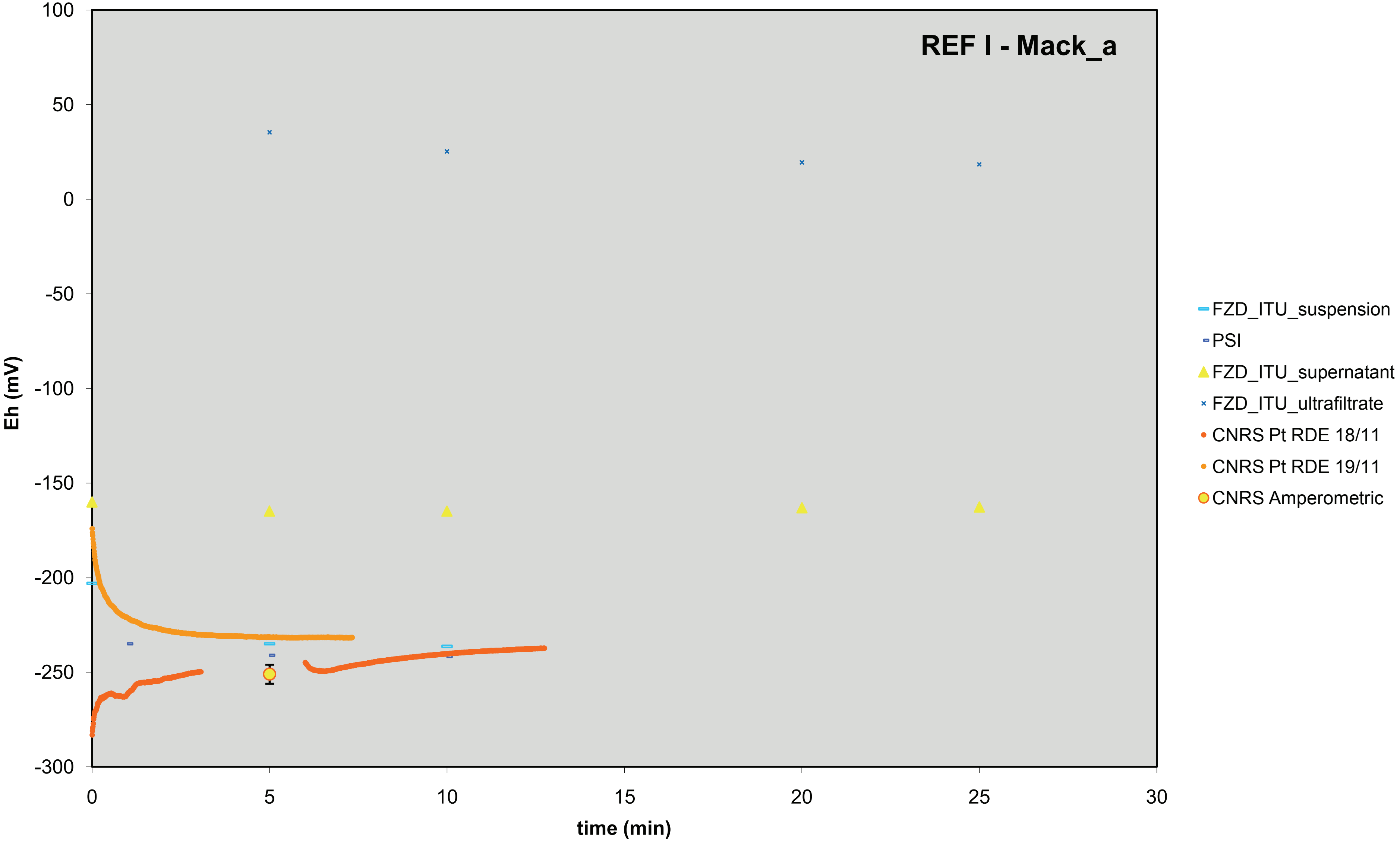
-100
-200
-300
-400
-500
-600
time (min)
0
5
10
15
20
25
30
35
40
45
50
◆ Amphos I
▭ FZD_ITU_suspension
▭ PSI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50
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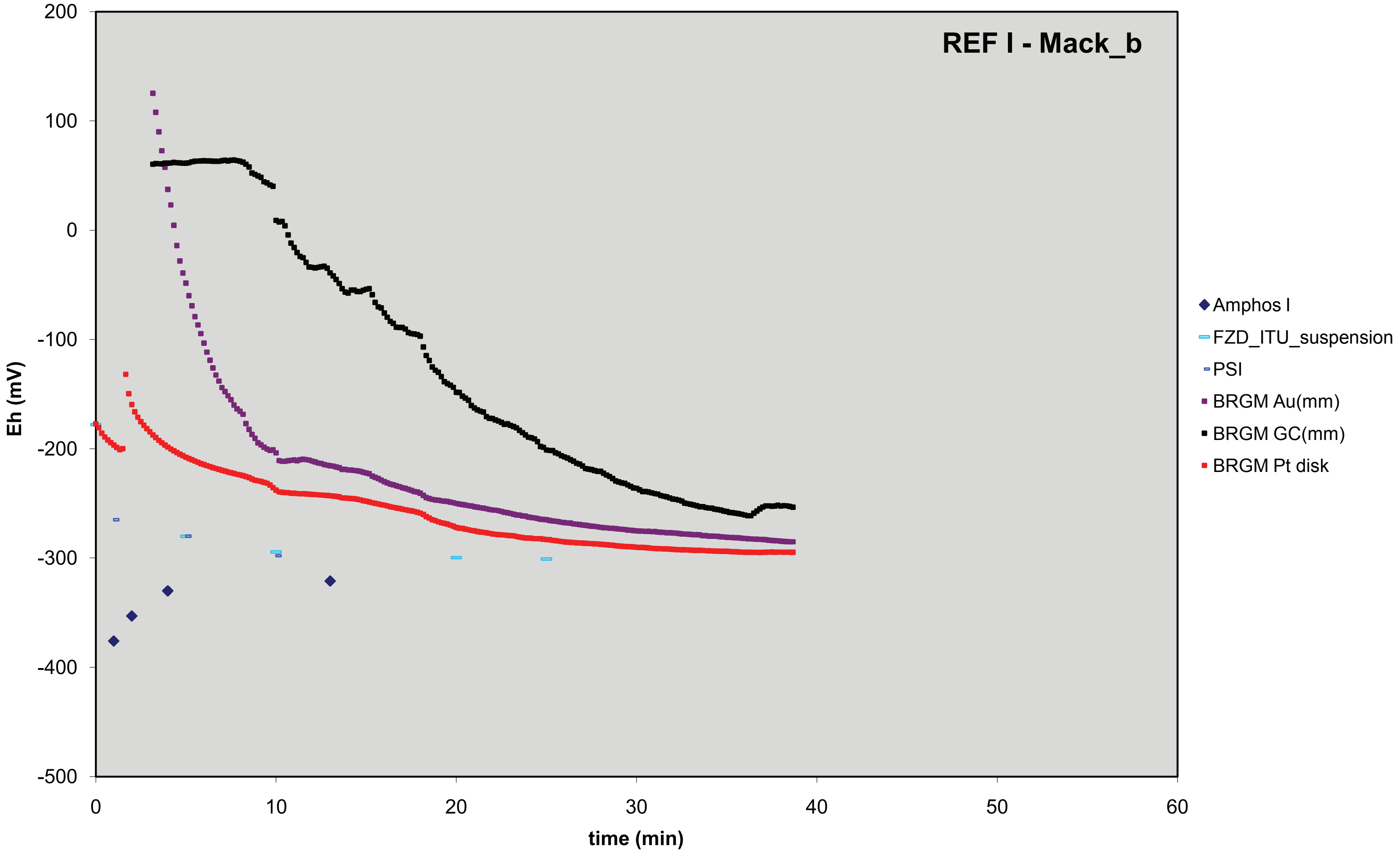
-50
-100
-150
-200
-250
-300
0
5
10
15
20
25
30
time (min)
FZD_ITU_suspension
PSI
FZD_ITU_supernatant
FZD_ITU_ultrafiltrate
CNRS Pt RDE 18/11
CNRS Pt RDE 19/11
CNRS Amperometric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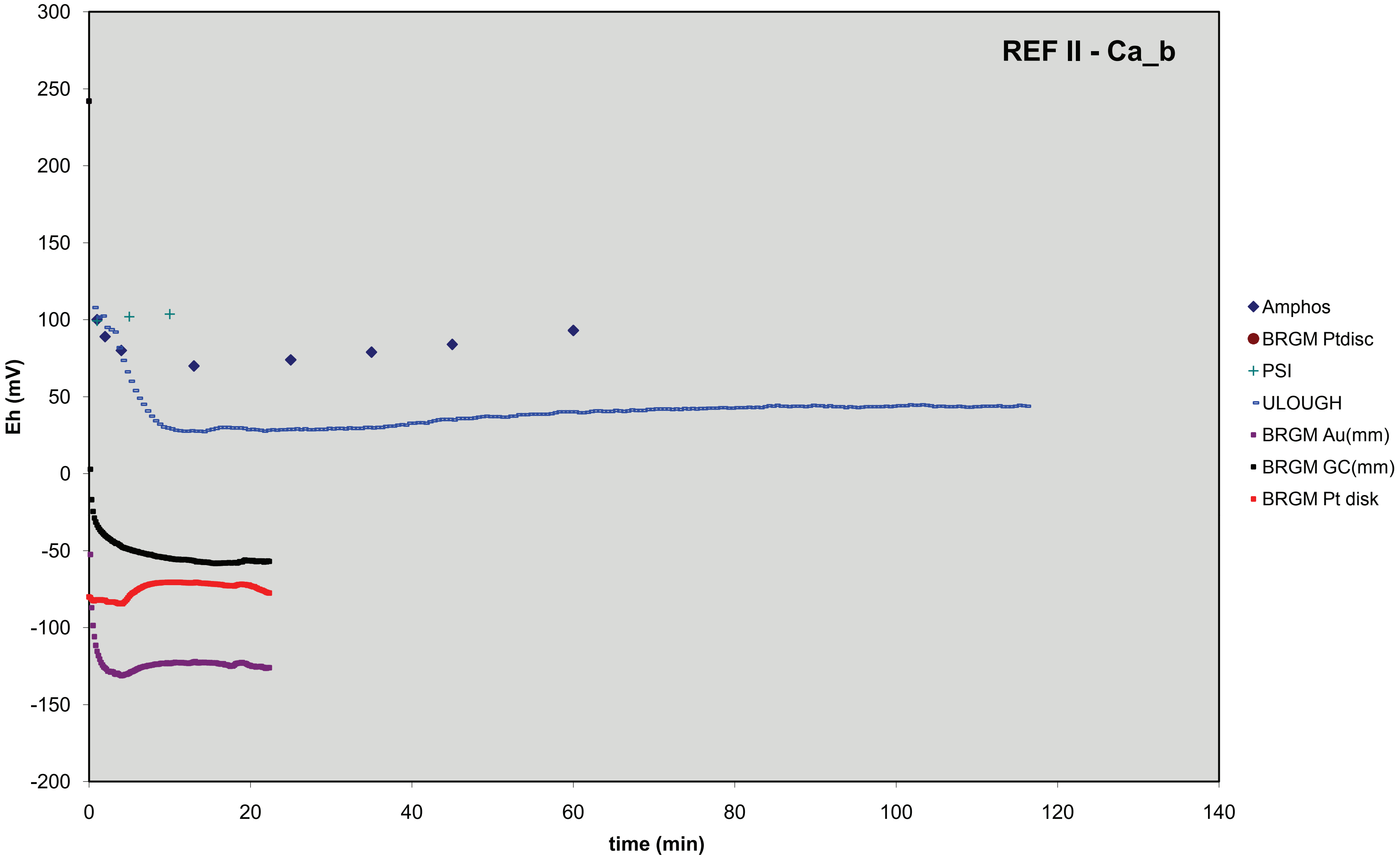
0
-100
-200
-300
-400
-500
0
10
20
30
40
50
60
time (min)
Amphos I
FZD_ITU_suspension
PSI
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk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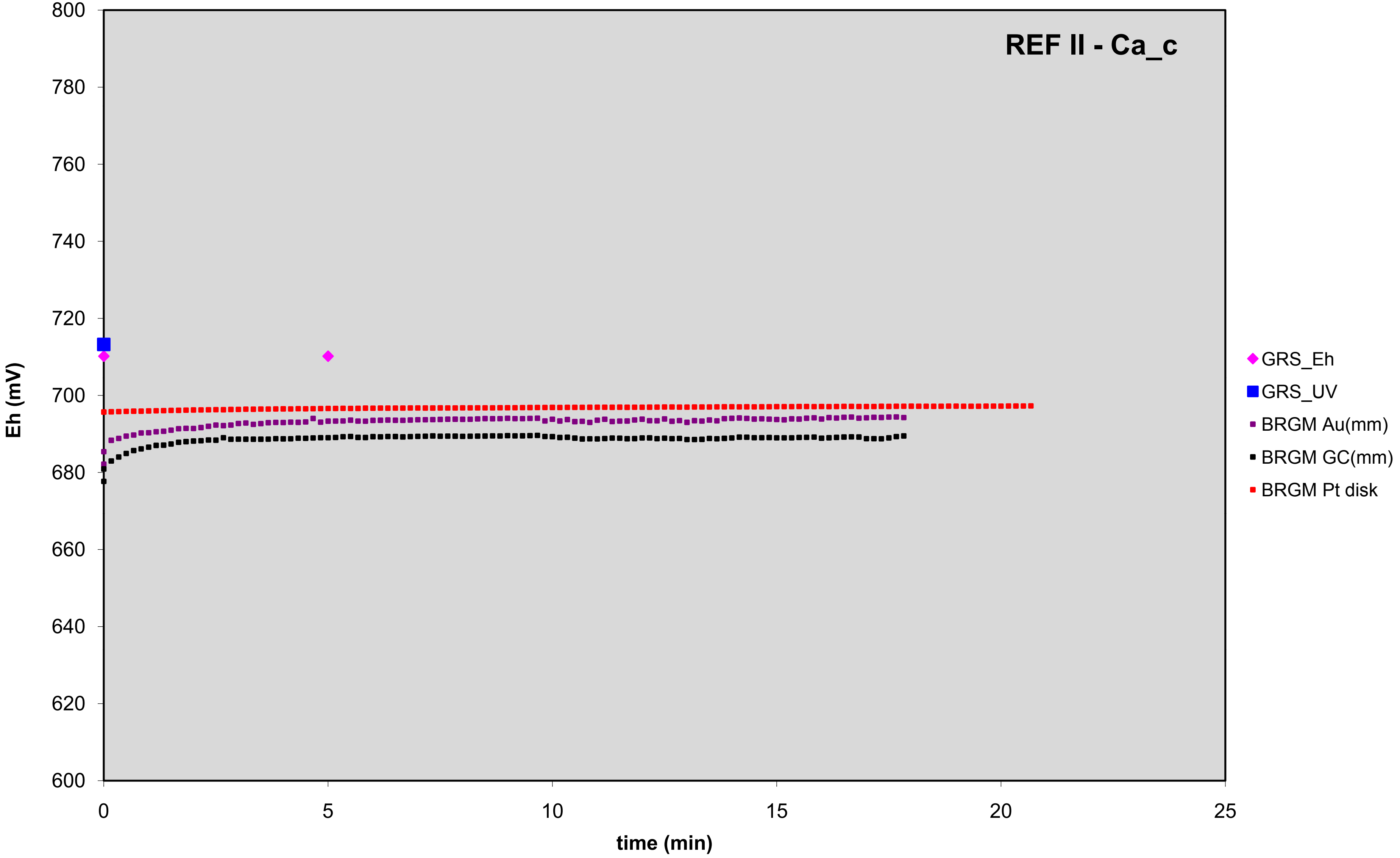
250
200
150
100
50
0
-50
-100
-150
-200
time (min)
0
20
40
60
80
100
120
140
Amphos
BRGM Ptdisc
PSI
ULOUGH
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk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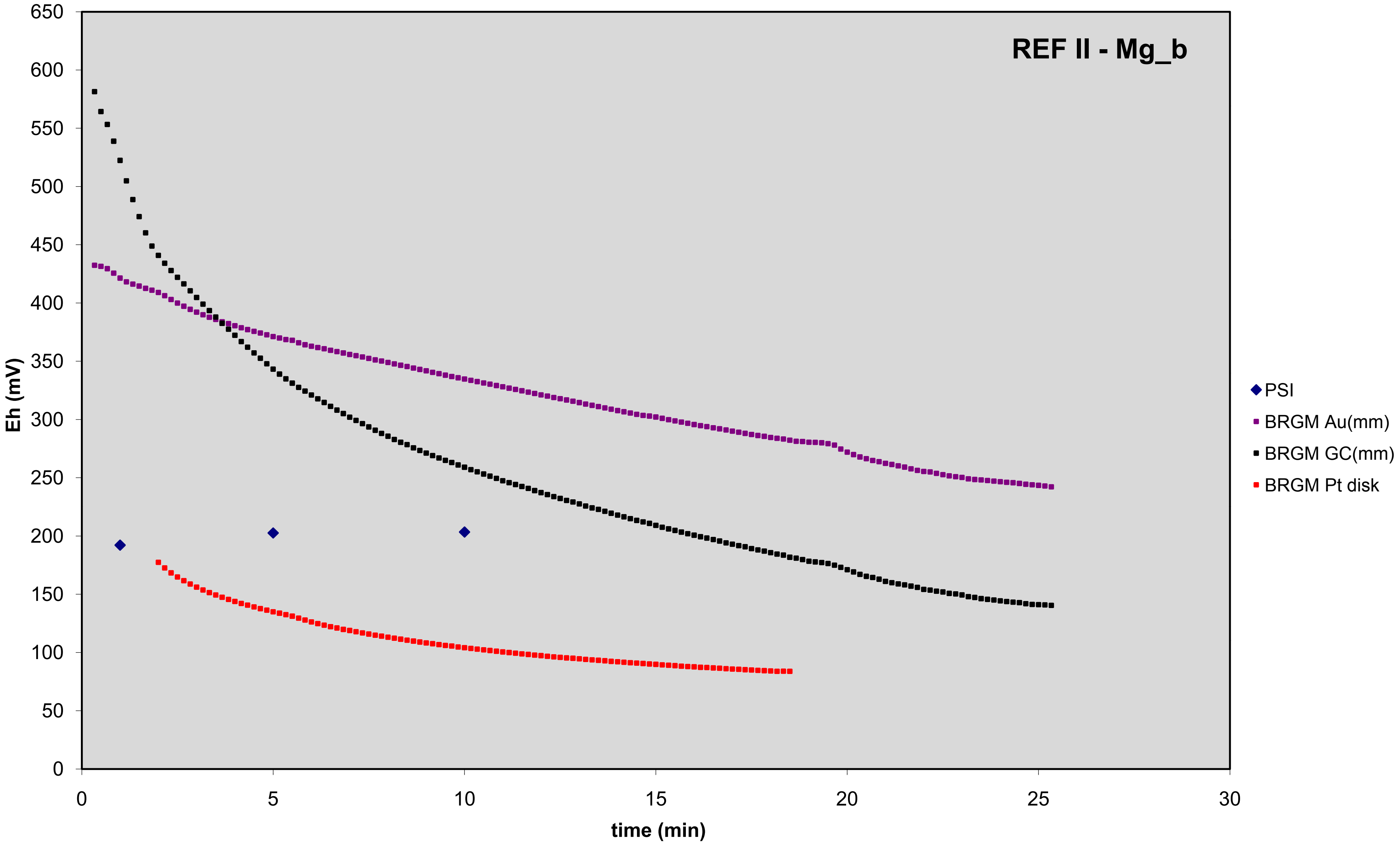
780
760
740
720
700
680
660
640
620
600
0
5
10
15
20
25
time (min)
◆ GRS_Eh
■ GRS_UV
▪ BRGM Au(mm)
▪ BRGM GC(mm)
▪ BRGM Pt disk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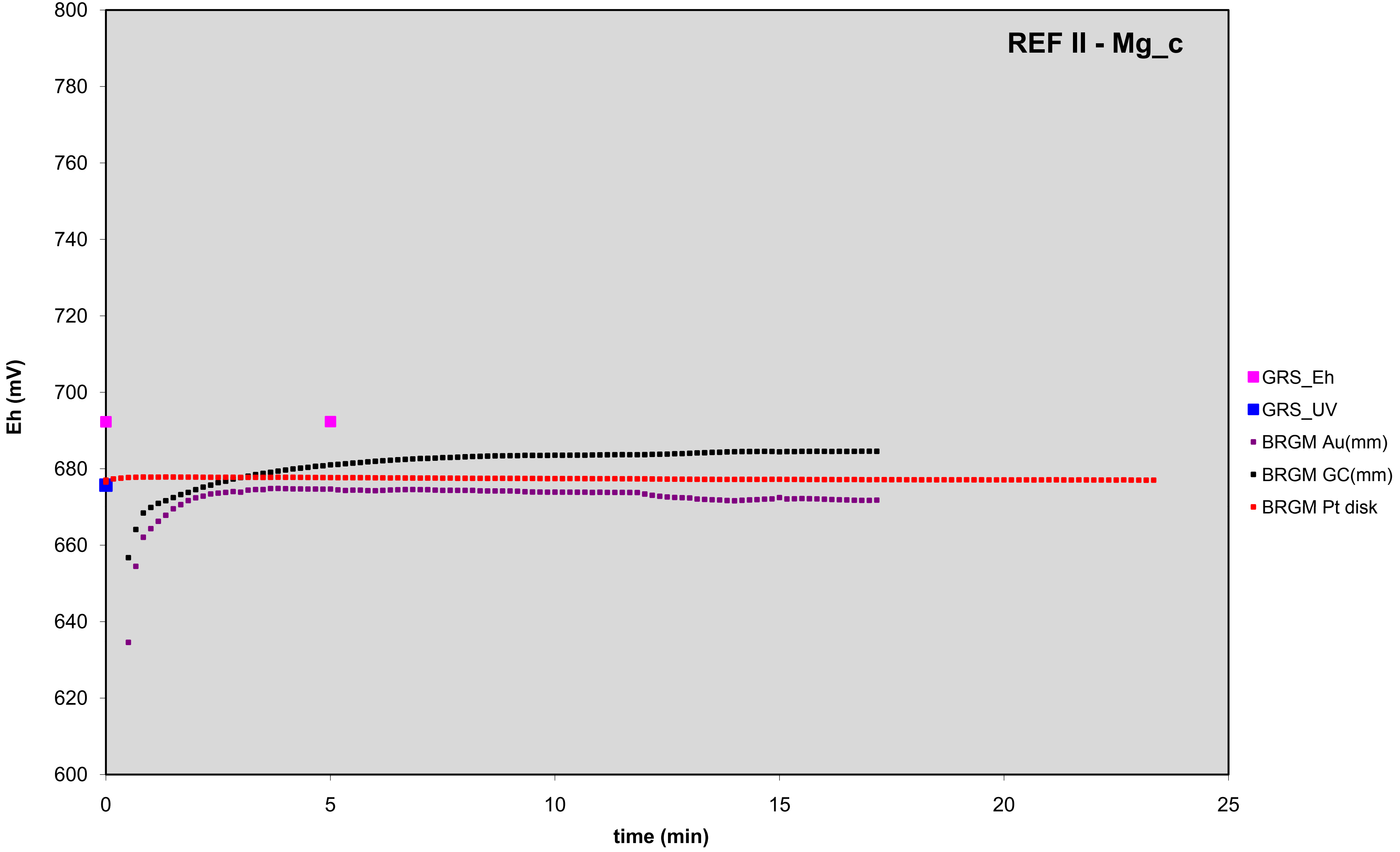
550
500
450
400
350
300
250
200
150
100
50
0
time (min)
0
5
10
15
20
25
30
◆ PSI
▪ BRGM Au(mm)
▪ BRGM GC(mm)
▪ BRGM Pt disk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Eh (mV)
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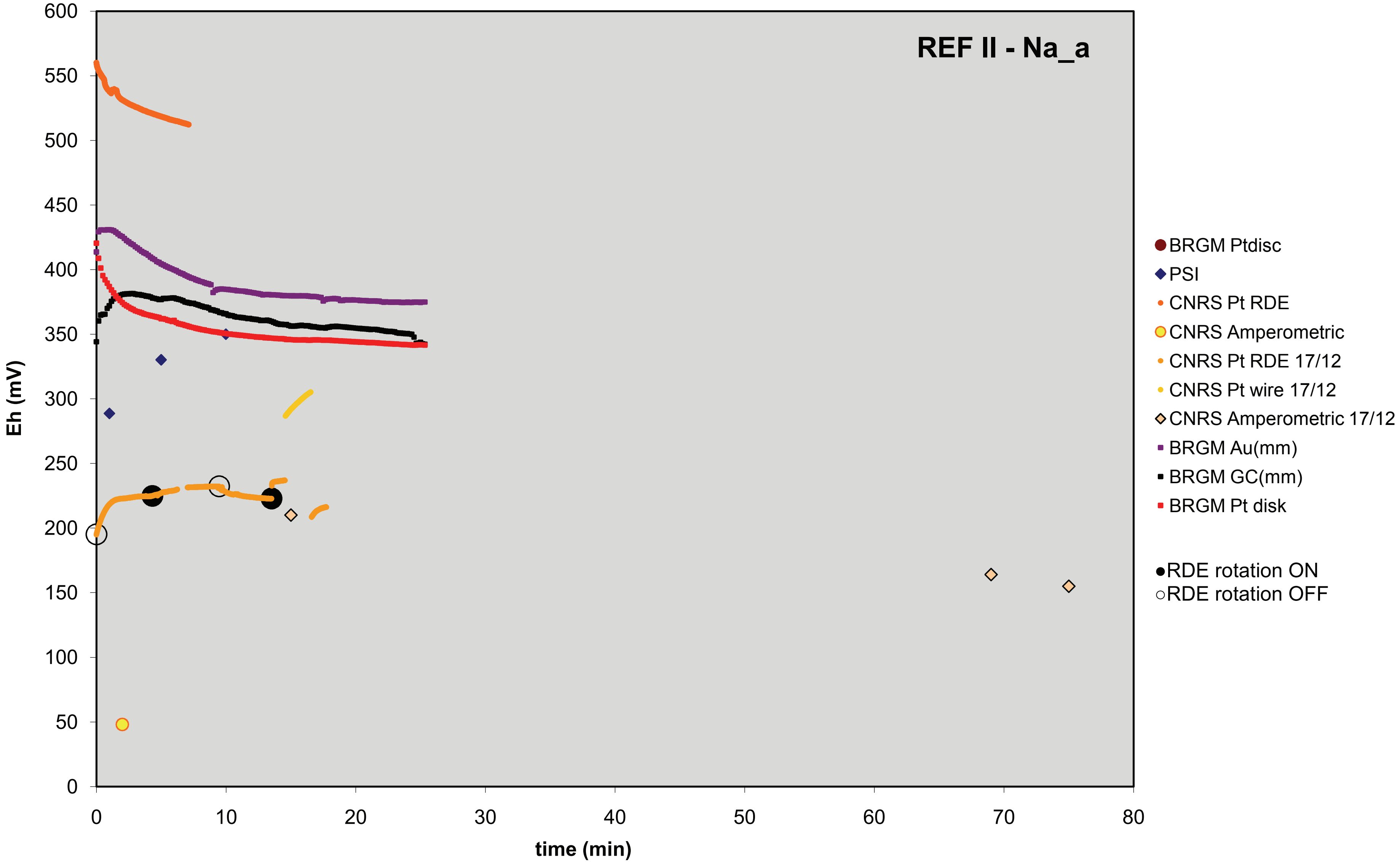
780
760
740
720
700
680
660
640
620
600
0
5
10
15
20
25
time (min)
GRS_Eh
GRS_UV
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk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Eh (mV)
time (min)
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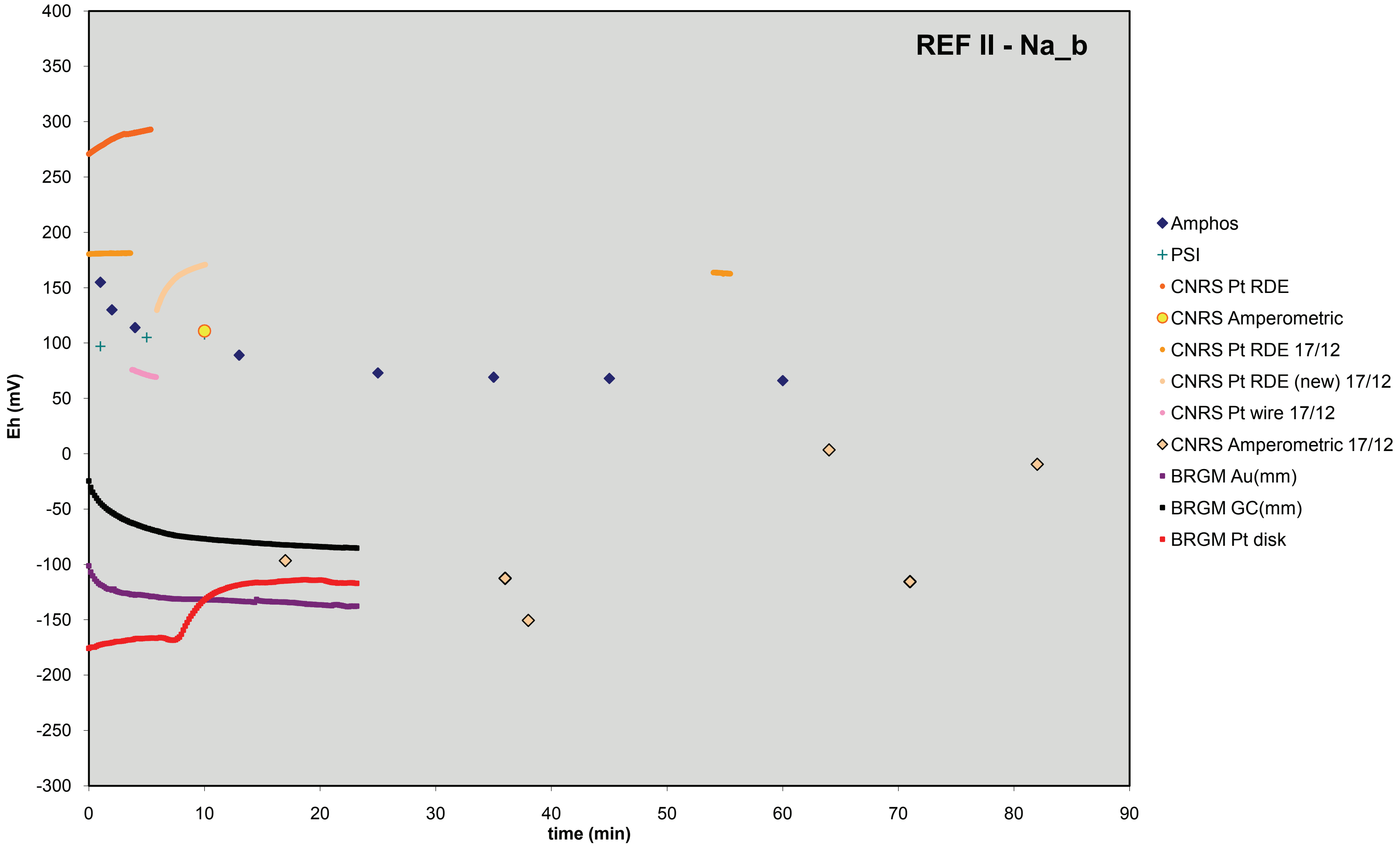
100
150
200
250
300
350
400
450
500
550
600
0
10
20
30
40
50
60
70
80
● BRGM Ptdisc
◆ PSI
● CNRS Pt RDE
○ CNRS Amperometric
● CNRS Pt RDE 17/12
● CNRS Pt wire 17/12
◇ CNRS Amperometric 17/12
■ BRGM Au(mm)
■ BRGM GC(mm)
■ BRGM Pt disk
● RDE rotation ON
○ RDE rotation OFF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Eh (mV)
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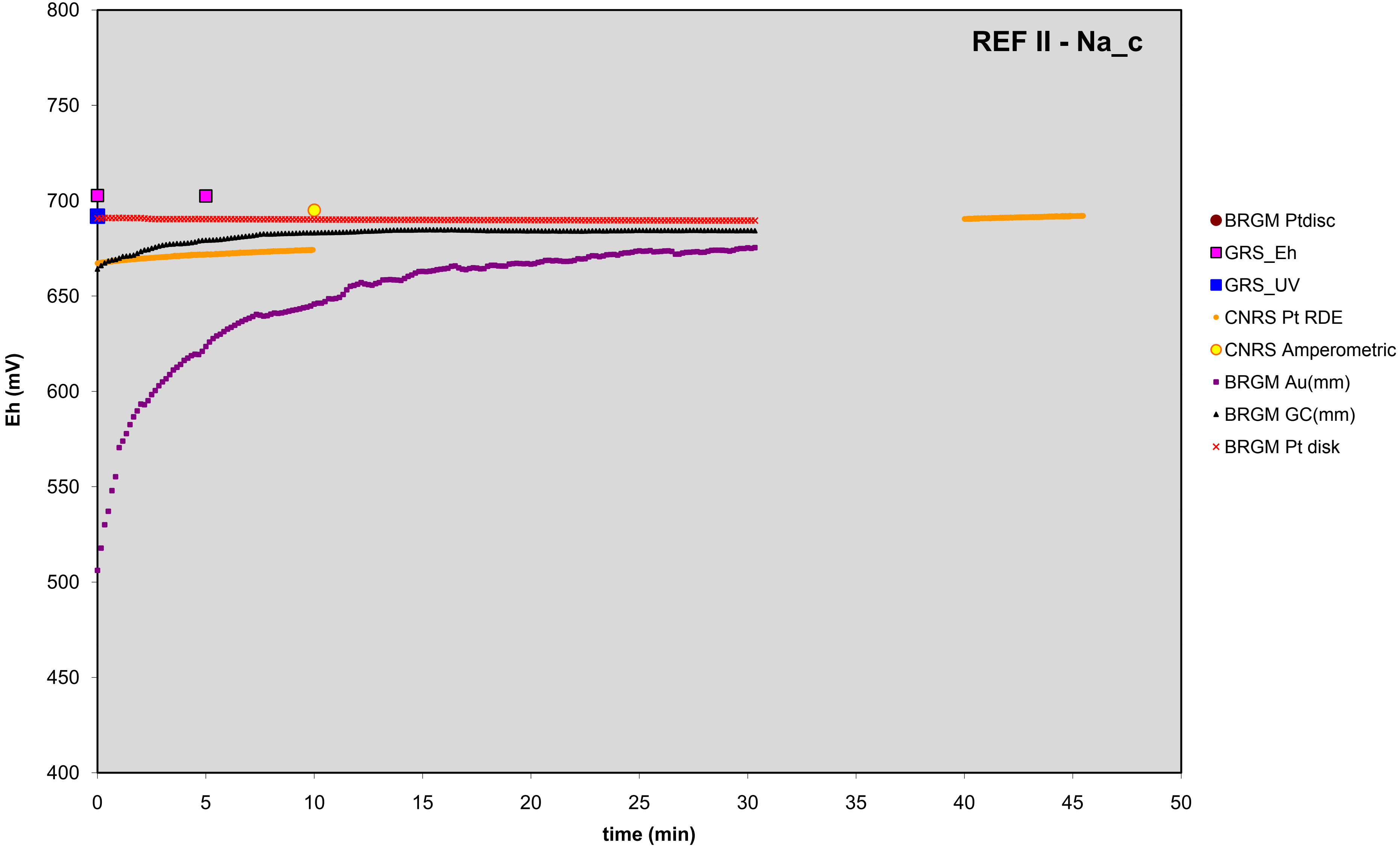
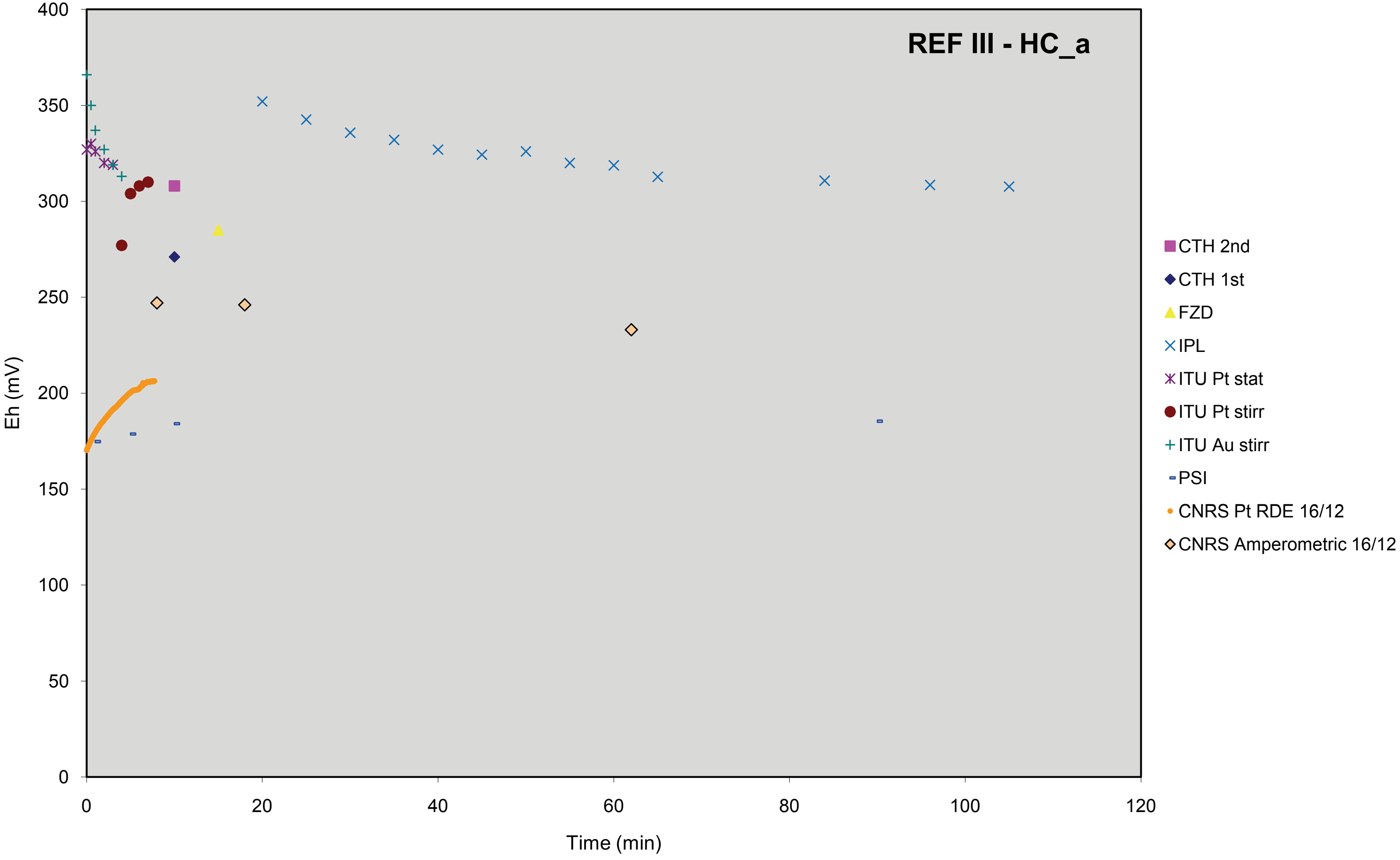
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
time (min)
0
10
20
30
40
50
60
70
80
90
◆ Amphos
+ PSI
● CNRS Pt RDE
○ CNRS Amperometric
● CNRS Pt RDE 17/12
● CNRS Pt RDE (new) 17/12
● CNRS Pt wire 17/12
◇ CNRS Amperometric 17/12
■ BRGM Au(mm)
■ BRGM GC(mm)
■ BRGM Pt disk


REF II - Na_c
Eh (mV)
800
750
700
650
600
550
500
450
400
0
5
10
15
20
25
30
35
40
45
50
time (min)
BRGM Ptdisc
GRS_Eh
GRS_UV
CNRS Pt RDE
CNRS Amperometric
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk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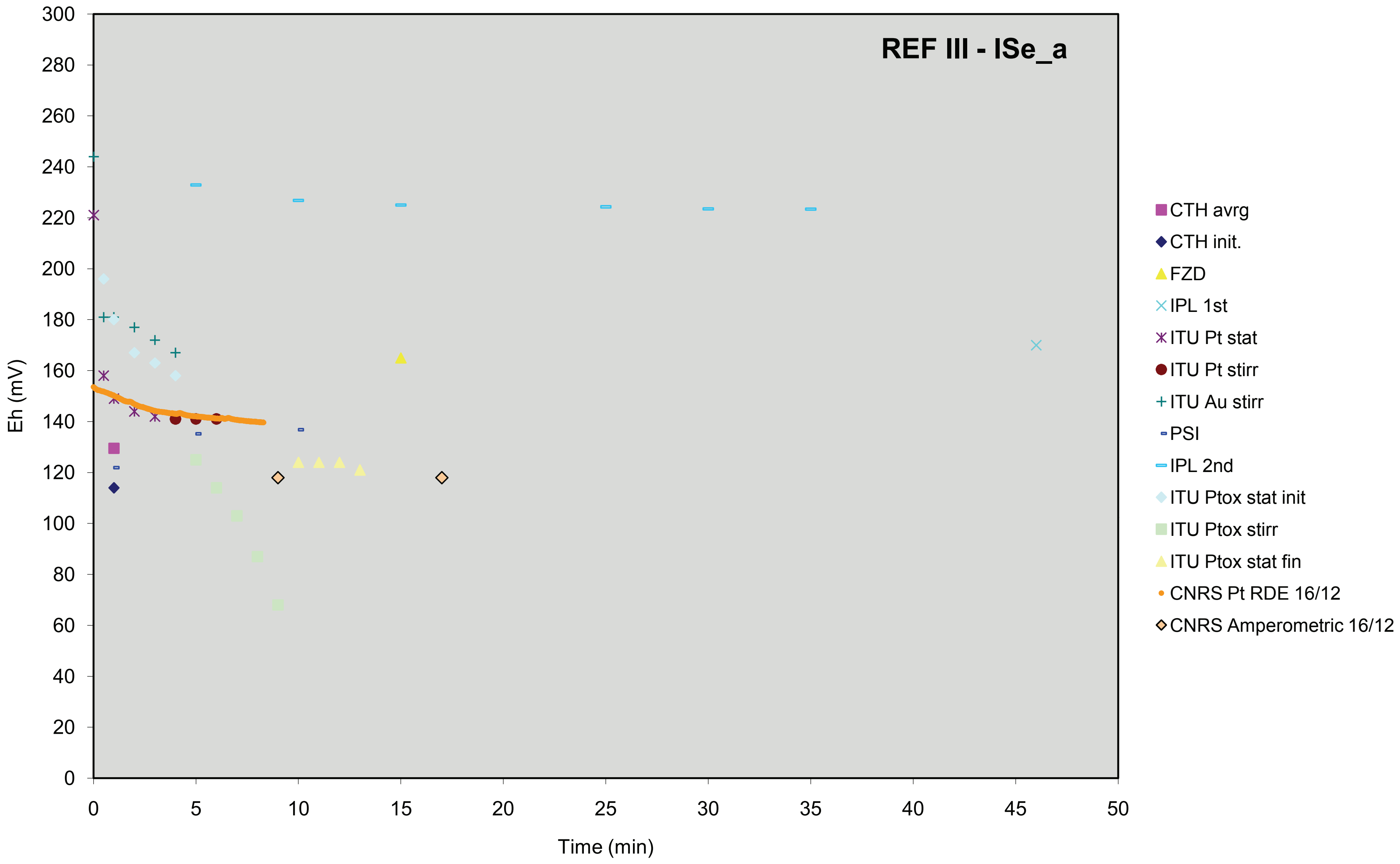
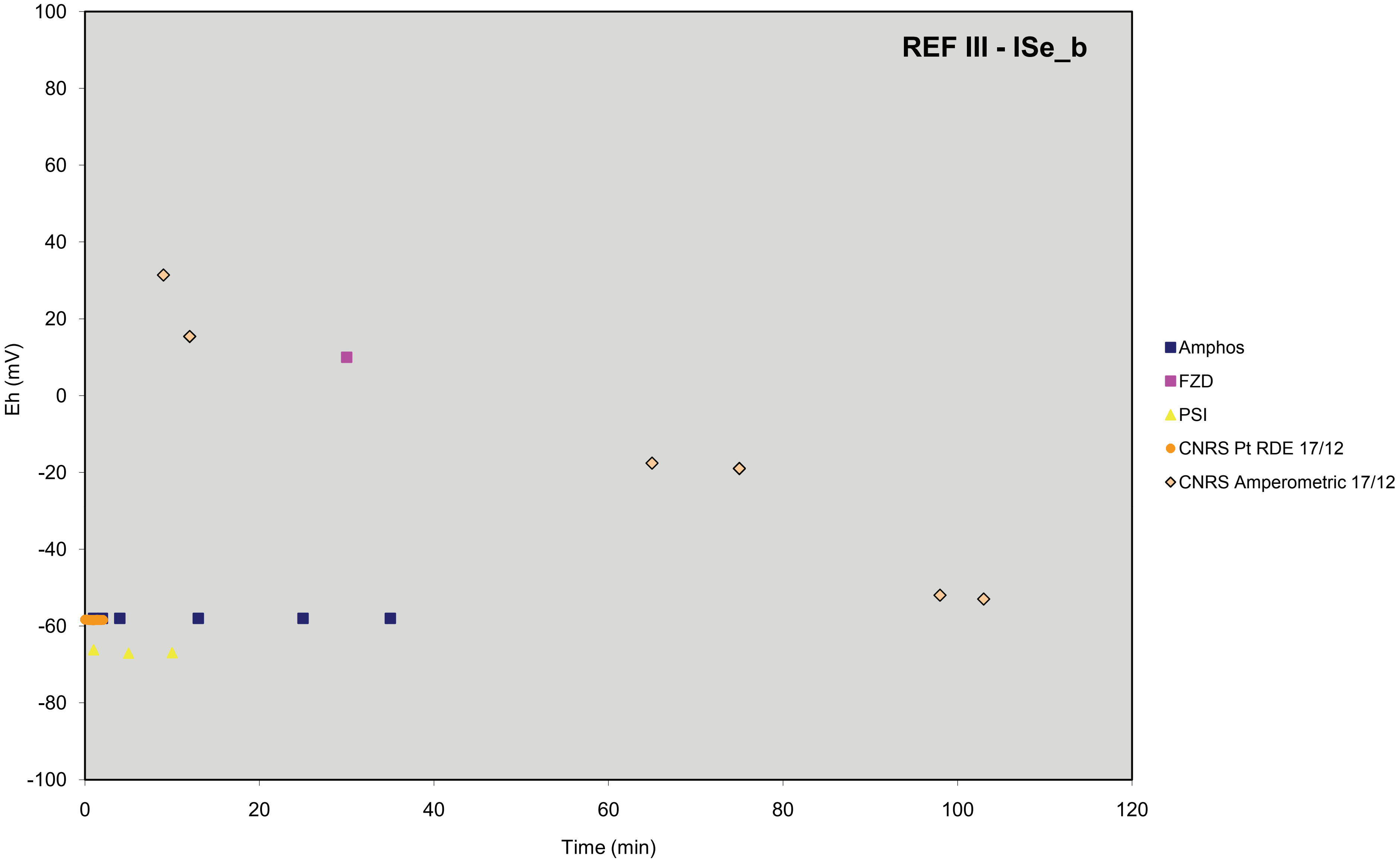
Eh (mV)
Time (min)
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
120
CTH 2nd
CTH 1st
FZD
IPL
ITU Pt stat
ITU Pt stirr
ITU Au stirr
PSI
CNRS Pt RDE 16/12
CNRS Amperometric 16/12


REF III - ISe_a
Eh (mV)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
Time (min)
0
5
10
15
20
25
30
35
40
45
50
CTH avrg
CTH init.
FZD
IPL 1st
ITU Pt stat
ITU Pt stirr
ITU Au stirr
PSI
IPL 2nd
ITU Ptox stat init
ITU Ptox stirr
ITU Ptox stat fin
CNRS Pt RDE 16/12
CNRS Amperometric 16/12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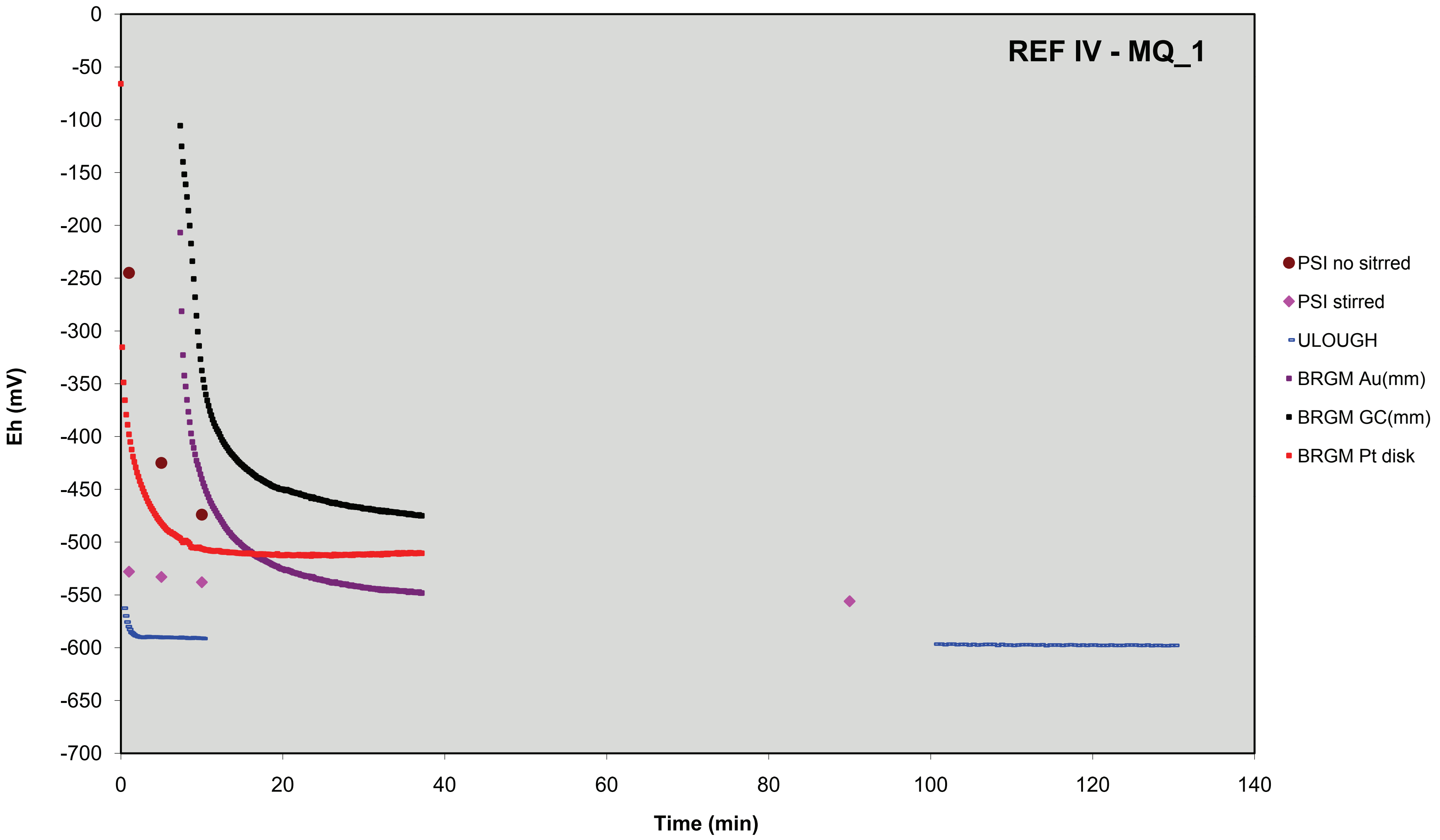
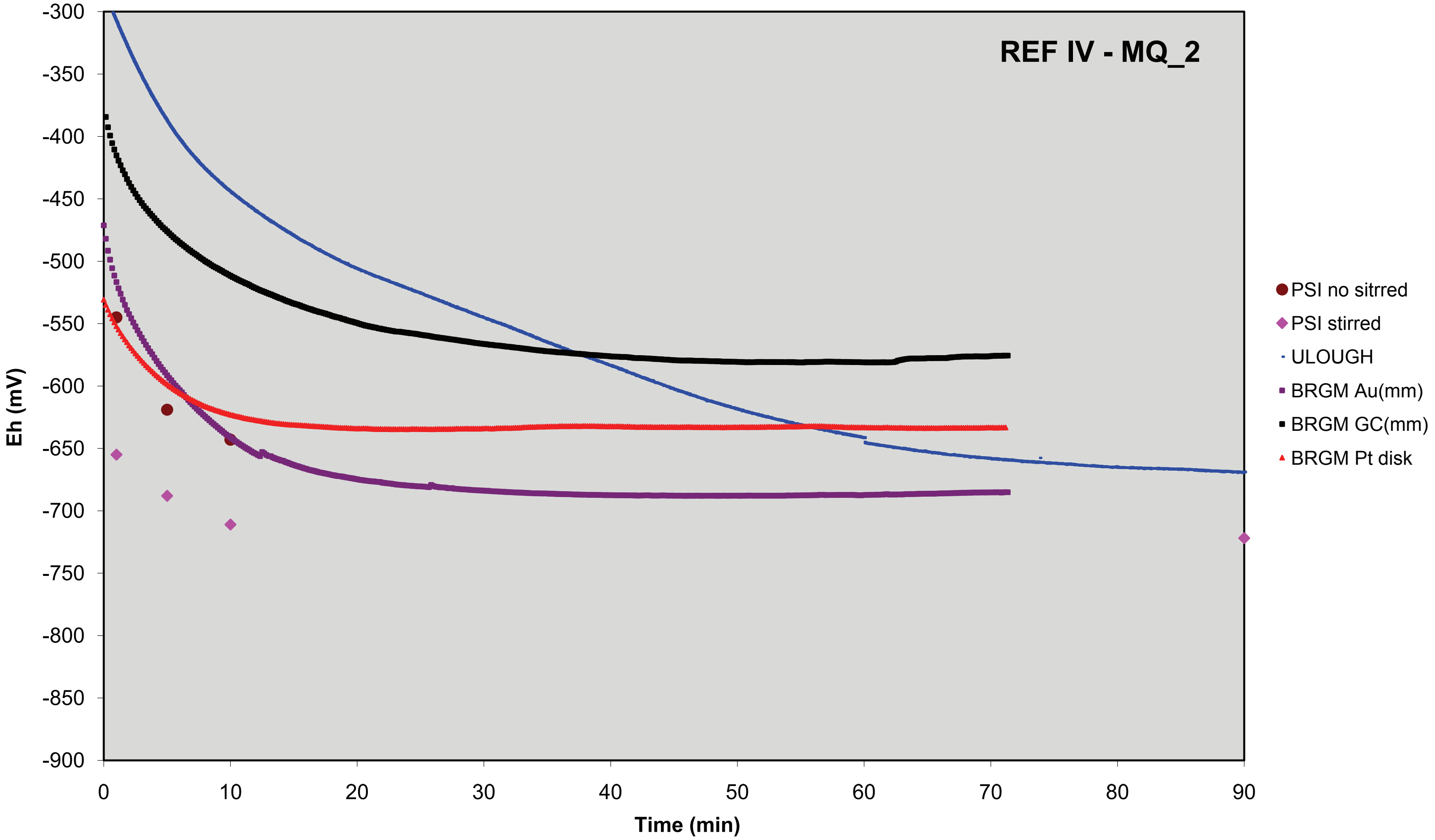
Eh (mV)
100
80
60
40
20
0
-20
-40
-60
-80
-100
0
20
40
60
80
100
120
Time (min)
■ Amphos
■ FZD
▲ PSI
● CNRS Pt RDE 17/12
◇ CNRS Amperometric 17/12


REF IV - MQ_1
Eh (mV)
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-500
-550
-600
-650
-700
0
20
40
60
80
100
120
140
Time (min)
PSI no sitrred
PSI stirred
ULOUGH
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk


REF IV - MQ_2
Eh (mV)
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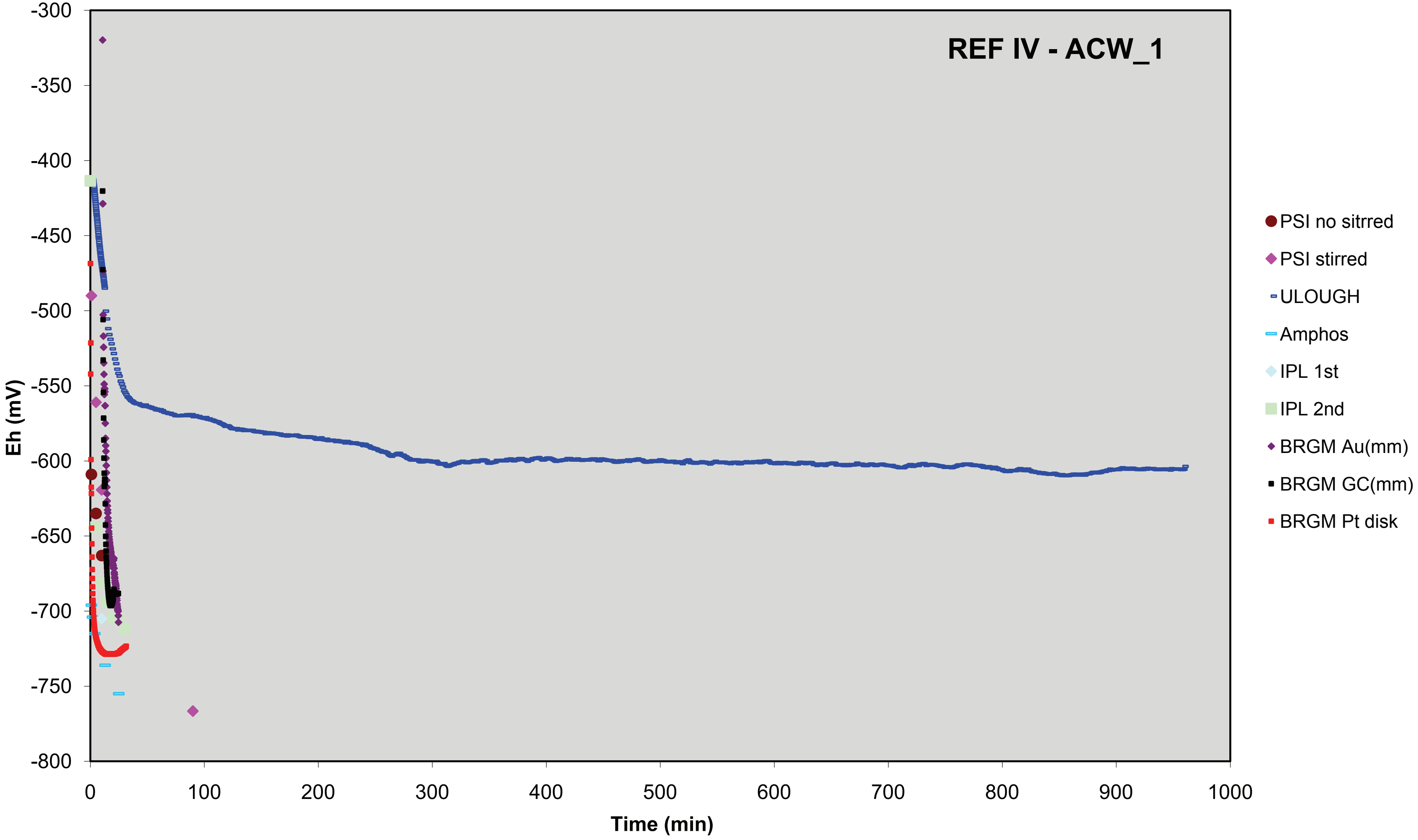
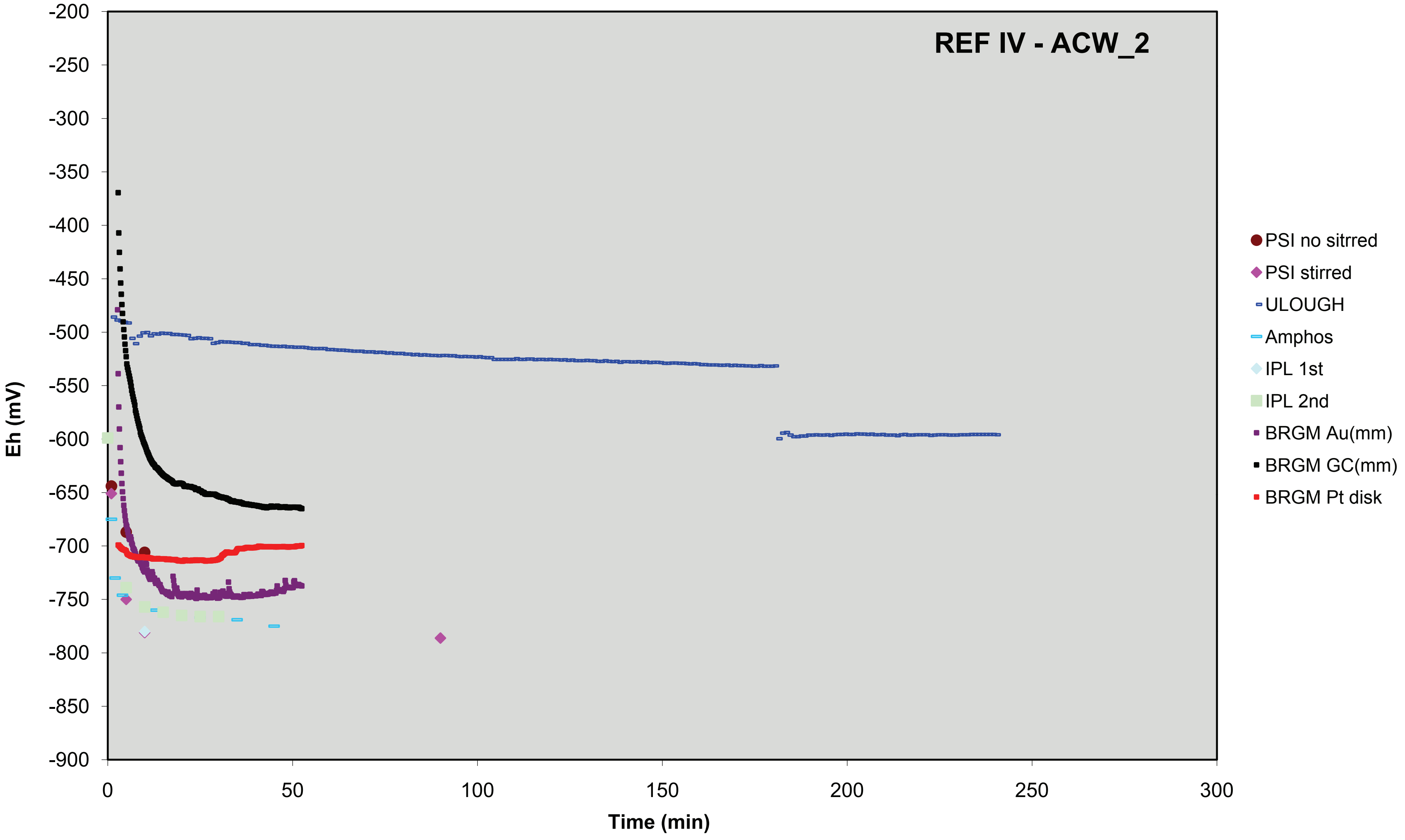
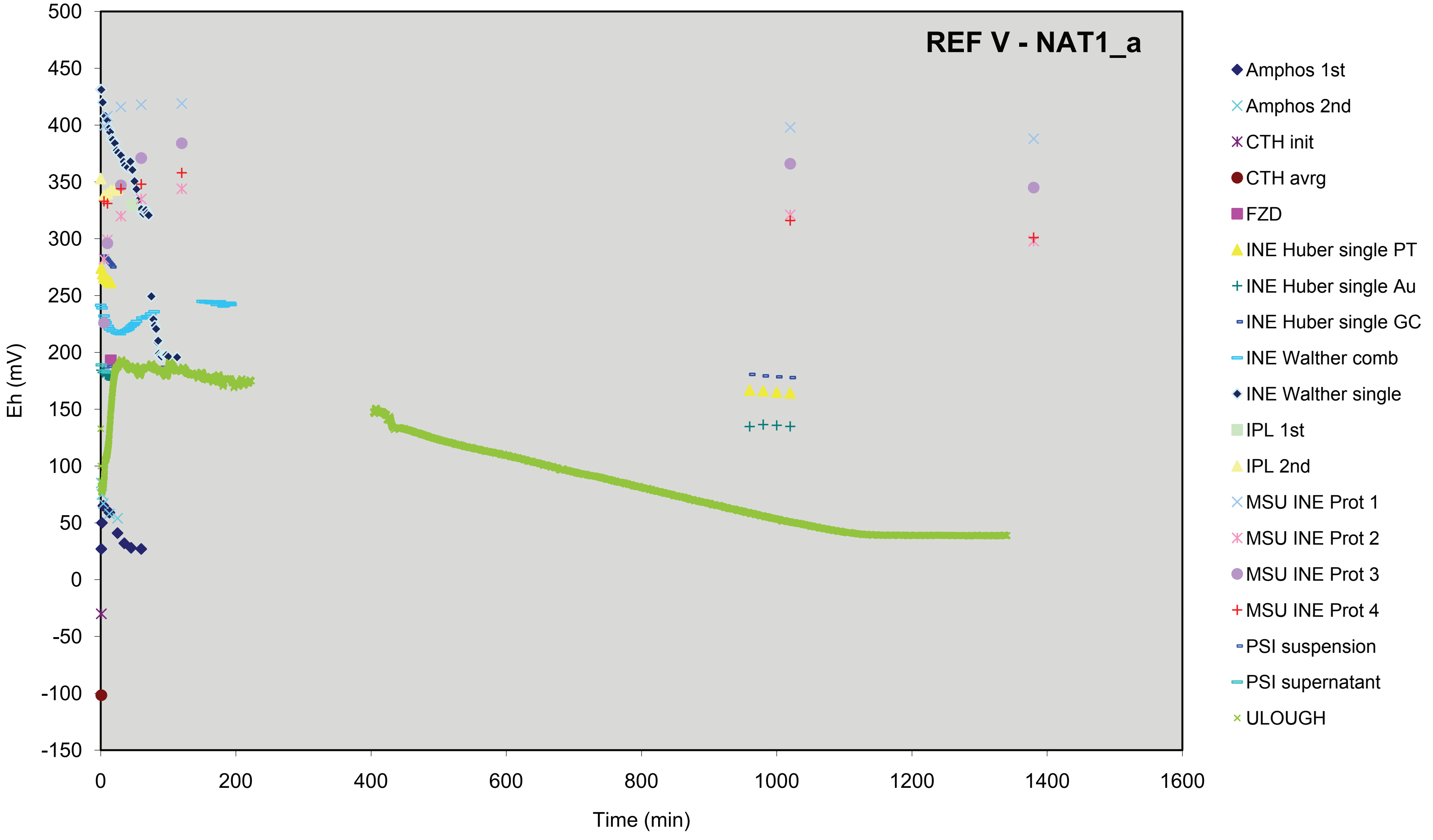
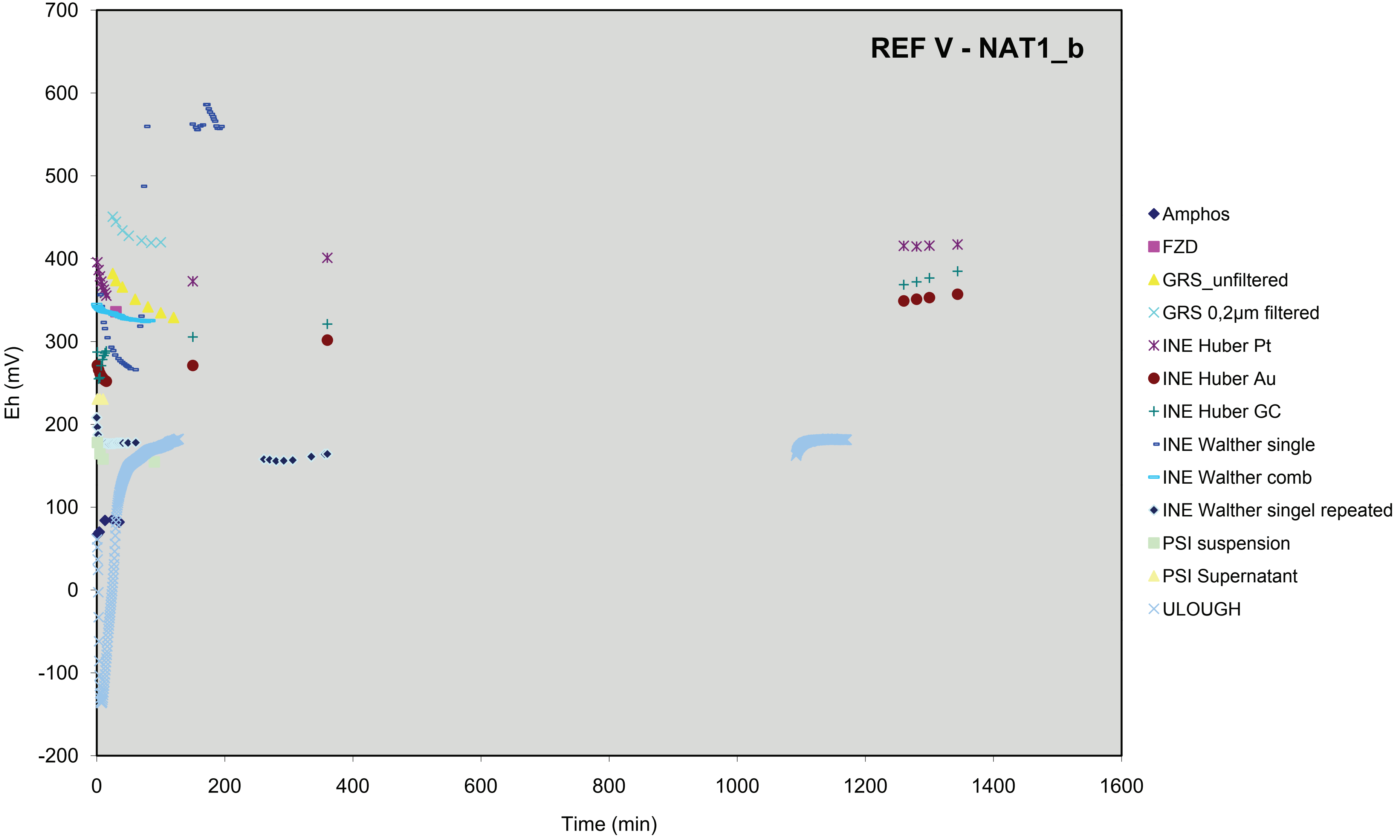
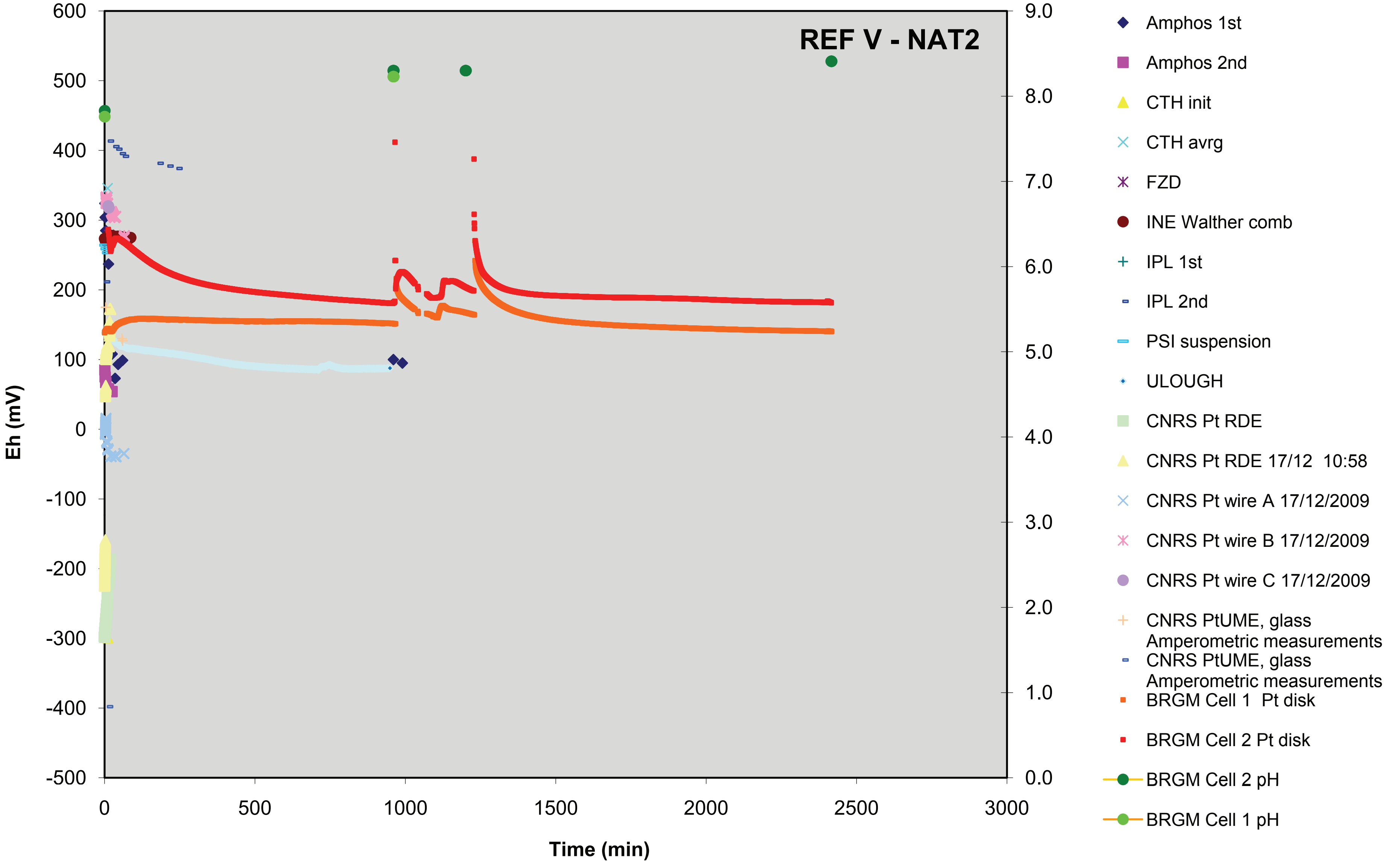
-350
-400
-450
-500
-550
-600
-650
-700
-750
-800
-850
-900
0
10
20
30
40
50
60
70
80
90
Time (min)
PSI no sitrred
PSI stirred
ULOUGH
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk

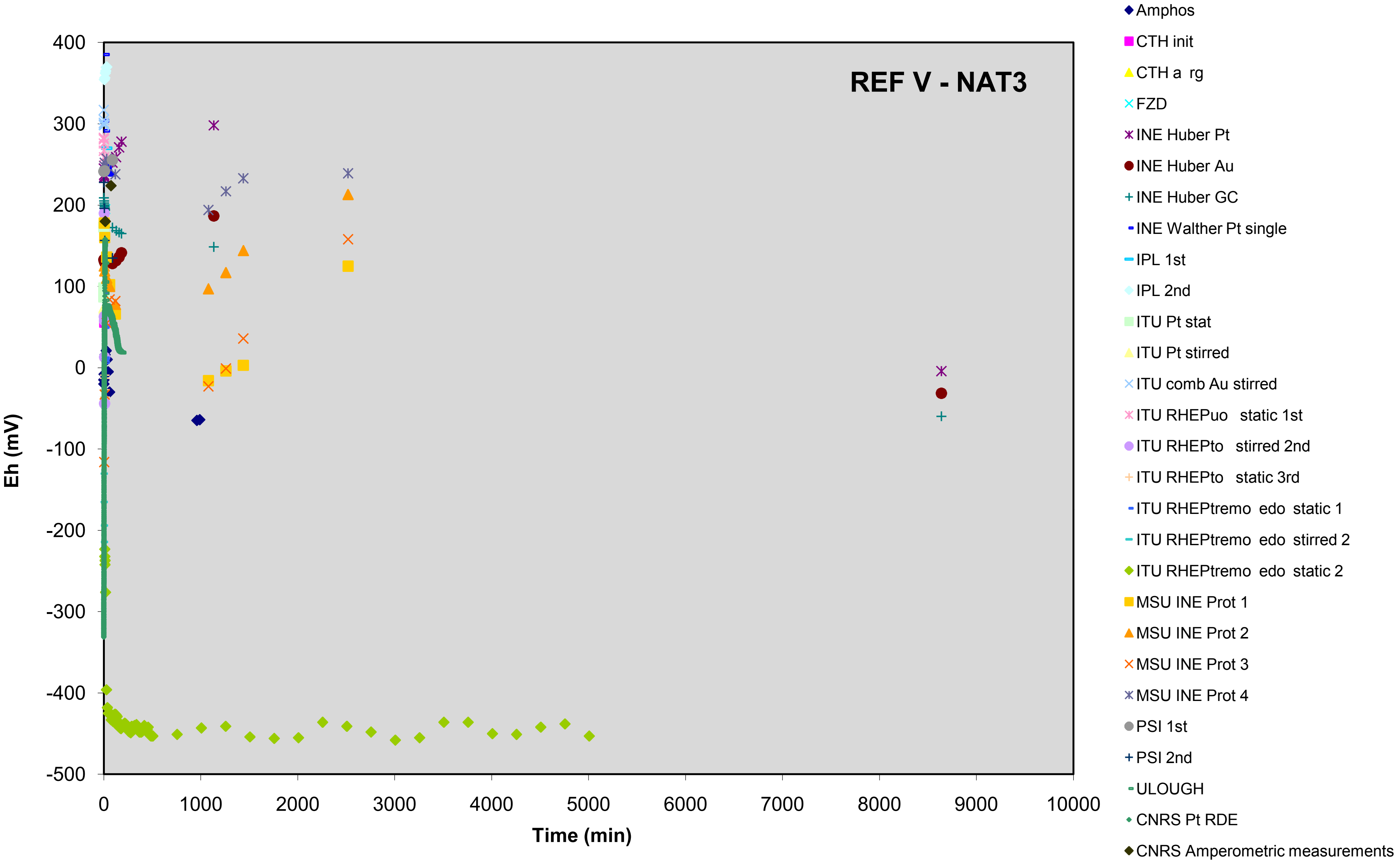

REF IV - ACW_1
Eh (mV)
Time (min)
-300
-350
-400
-450
-500
-550
-600
-650
-700
-750
-800
0
100
200
300
400
500
600
700
800
900
1000
PSI no sitrred
PSI stirred
ULOUGH
Amphos
IPL 1st
IPL 2nd
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk

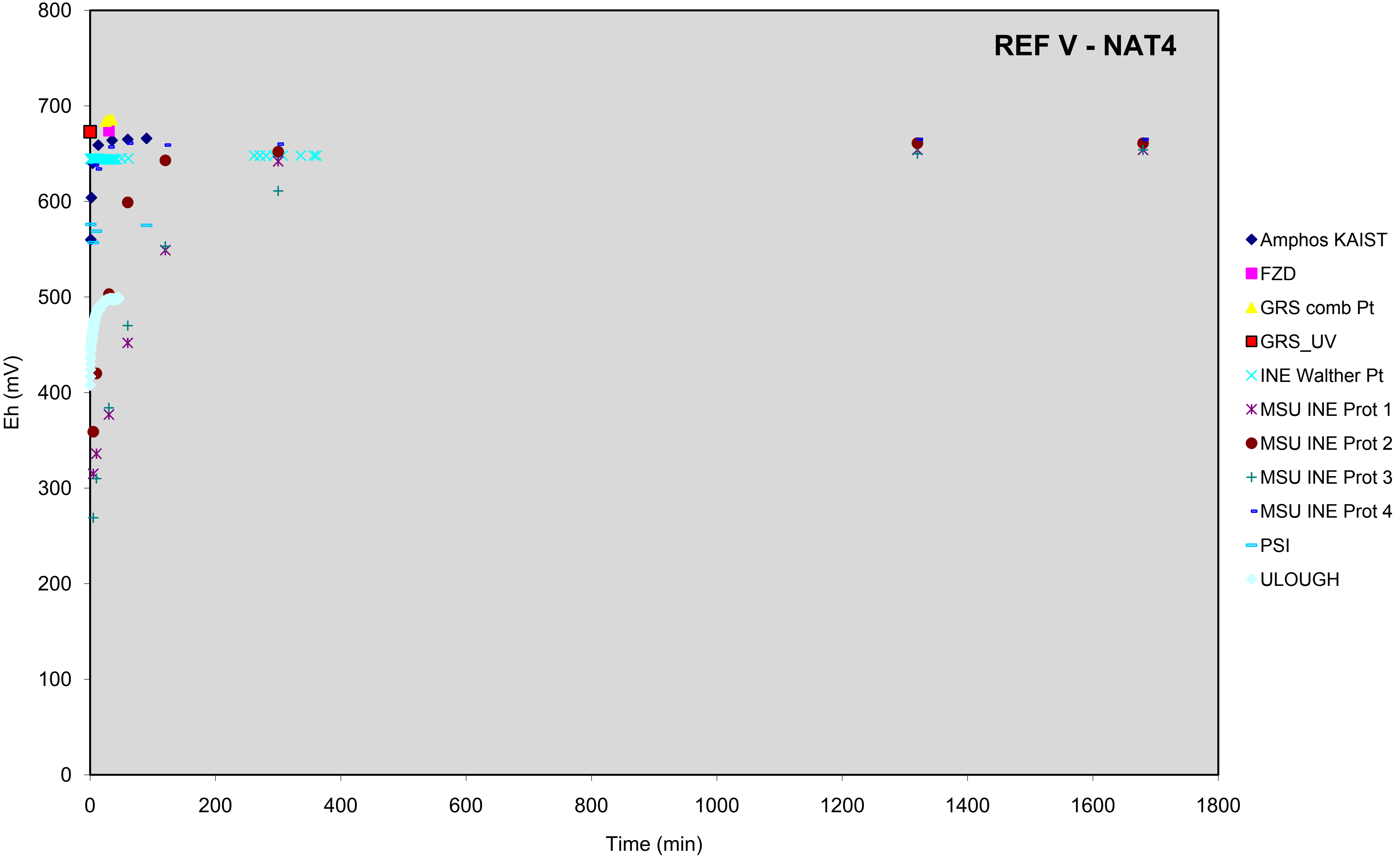

REF IV - ACW_2
Eh (mV)
-200
-250
-300
-350
-400
-450
-500
-550
-600
-650
-700
-750
-800
-850
-900
Time (min)
0
50
100
150
200
250
300
PSI no sitrred
PSI stirred
ULOUGH
Amphos
IPL 1st
IPL 2nd
BRGM Au(mm)
BRGM GC(mm)
BRGM Pt disk


REF V - NAT1_a
Eh (mV)
Time (min)
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
0
200
400
600
800
1000
1200
1400
1600
Amphos 1st
Amphos 2nd
CTH init
CTH avrg
FZD
INE Huber single PT
INE Huber single Au
INE Huber single GC
INE Walther comb
INE Walther single
IPL 1st
IPL 2nd
MSU INE Prot 1
MSU INE Prot 2
MSU INE Prot 3
MSU INE Prot 4
PSI suspension
PSI supernatant
ULOUGH


REF V - NAT1_b
Eh (mV)
700
600
500
400
300
200
100
0
-100
-200
Time (min)
0
200
400
600
800
1000
1200
1400
1600
Amphos
FZD
GRS_unfiltered
GRS 0,2µm filtered
INE Huber Pt
INE Huber Au
INE Huber GC
INE Walther single
INE Walther comb
INE Walther singel repeated
PSI suspension
PSI Supernatant
ULOUGH


REF V - NAT2
Eh (mV)
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
500
1000
1500
2000
2500
3000
Time (min)
Amphos 1st
Amphos 2nd
CTH init
CTH avrg
FZD
INE Walther comb
IPL 1st
IPL 2nd
PSI suspension
ULOUGH
CNRS Pt RDE
CNRS Pt RDE 17/12 10:58
CNRS Pt wire A 17/12/2009
CNRS Pt wire B 17/12/2009
CNRS Pt wire C 17/12/2009
CNRS PtUME, glass Amperometric measurements
CNRS PtUME, glass Amperometric measurements
BRGM Cell 1 Pt disk
BRGM Cell 2 Pt disk
BRGM Cell 2 pH
BRGM Cell 1 pH


REF V - NAT3
Eh (mV)
400
300
200
100
0
-100
-200
-300
-400
-500
Time (min)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
Amphos
CTH init
CTH a rg
FZD
INE Huber Pt
INE Huber Au
INE Huber GC
INE Walther Pt single
IPL 1st
IPL 2nd
ITU Pt stat
ITU Pt stirred
ITU comb Au stirred
ITU RHEPuo static 1st
ITU RHEPto stirred 2nd
ITU RHEPto static 3rd
ITU RHEPtremo edo static 1
ITU RHEPtremo edo stirred 2
ITU RHEPtremo edo static 2
MSU INE Prot 1
MSU INE Prot 2
MSU INE Prot 3
MSU INE Prot 4
PSI 1st
PSI 2nd
ULOUGH
CNRS Pt RDE
CNRS Amperometric measurements



REF V - NAT4
Eh (mV)
800
700
600
500
400
300
200
100
0
Time (min)
0
200
400
600
800
1000
1200
1400
1600
1800
Amphos KAIST
FZD
GRS comb Pt
GRS_UV
INE Walther Pt
MSU INE Prot 1
MSU INE Prot 2
MSU INE Prot 3
MSU INE Prot 4
PSI
ULOUGH

Reports from individual partners – Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems

FP 7 EURATOM Collaborative Project „Redox Phenomena Controlling Systems“

The reports below were prepared by the individual groups participating in ICE:

Amphos 21 – KAIST

O. Riba, J. Y. Oh, M. Grivé. „*Redox potential measurements to assess the equilibration times of the electrode“.*

BRGM

S. Betelu, C. Tournassat, I. Ignatiadis. „*Redox potential measurements using different electrodes and comparison with equilibrium potential computed by geochemical modelling*“

CNRS

M. Perdicakis, C. Streiff. „*Application of the potentiometric and the amperometric methods for the redox potential determination*“

CTH

S. Allard, C. Ekberg, S. Holgersson, G. Skarnemark, K. Spahiu, A. Ödegaard-Jensen. „*Agreement between measured Eh and quantification of oxidation states*“.

FZD – ROBL

- E. Krawczyk-Bärsch. „*Report and evaluation of the redox potential measurements during the Intercomparison Exercise of ReCosy“.*

- D. Fellhauer (ITU), R. Kirsch. „*Comparing the impact of measuring in suspension, after centrifugation and after ultra-filtration on the obtained pe and pH values and comparing with pe-values calculated from photo-spectrometrically determined Fe(II) and Fe(III) concentrations“*

GRS

B. Bischofer, T. Scharge, S. Hagemann. „*Redox Measurements of Saline Samples by Spectrophotometric and Potentiometric Methods“.*

IPL

G. Lujaniene. „*Individual report by IPL*“.

JRC-ITU

D.H. Wegen, A. Seibert, P. Carbol. „*Uncertainties in Redox Potential Measurements Redox measurements carried out at ITU*“ (only available in the CD-version of the report, or by request to the authors - detlef.wegen@ec.europa.eu).

KIT-INE

- F. Huber, N. Müller, G. Buckau. „*Separation of drift on reference and active electrode*“

- M. Icker, C. Walther. „*Separation of drift on reference and active electrode*“

- V. Petrov (MSU), M. Böttle, M. Altmaier. „*Test of cleaning protocols for (Pt) combination electrodes*“

PSI-LES

J. Tits, X. Gaona. „*Measurement of redox potentials in reference solutions with a combined redox electrode. Effect of measurement time. Comparison with thermodynamic calculations*“.

TUG – INE – UKOE

B. Kuczewski, M. Lagos, C. M. Marquardt, E. Marosits, C. Dull. *Determination of redox species of iodine and iron with CE-ICP-MS*

ULOUG:

- S. L. Jain, M. Felipe-Sotelo. *ReCosy Intercomparison Exercise Workpackage 2*.
- M. Felipe-Sotelo. *ReCosy Intercomparison Exercise: Statistical analysis*.

UPPC

D. Steinbrück, M. U. Kumke. *Fiber-optical sensing of oxygen in reference and natural samples*.

TUG – INE – UKOE

B. Kuc e ski, M. Lagos, C. M. Marquardt, E. Marosits, C. Dull . *Determination of redox species of iodine and iron with CE-ICP-MS*

ULOUG:

- S. L. Jain, M. Felipe-Sotelo. *ReCosy Intercomparison Exercise Workpackage 2* .
- M. Felipe-Sotelo. *ReCosy Intercomparison Exercise: Statistical analysis* .

UPPC

D. Steinbr ck, M. U. Kumke. *Fiber-optical sensing of oxygen in reference and natural samples* .

ReCosy, Intercomparison Exercise

Within Workpackage 2 Development of redox determination methods

Redox potential measurements to assess the equilibration times of the electrode

Olga Riba, Jae Yong Oh, Mireia Grivé

Background and Objectives

The redox potential is one of the main parameters affecting the long-term release of some active radionuclides in nuclear waste disposal. There is still a lack of a definite adequate method to measure reliable redox potential of natural environments and in many cases measurements of redox potential in natural groundwater systems by redox active electrodes show drifts over an extended period of time. Different causes are associated with this drift, among them there is the transformation of the active electrode surface due to deposition of material on the surface of the electrode. In those cases when the experimental set up involves continuous redox measurements, leakage in or out through the reference electrode liquid junction can occur, changing the redox potential of the reference electrode.

The current study aims at assessing the different equilibration times for a conventional Pt electrode required for the measurement of redox potential of different solutions, including natural groundwaters. Most of the measurements were expanded up one hour and data was taken after 1 minute measuring time.

Experimental method and approach

The redox potential of the samples specified in the *solutions measured* section was measured with a combined Pt working electrode equipped with a Ag/AgCl reference electrode and 3M KCl as electrolyte (HAMILTON Glass ORD, ref. number: 238145/07). The potentiometer used in the exercise was a Microprocessor pH meter pH 3000 WTW.

The external electrolyte compartment of the electrode was left uncapped to avoid sample solution diffusing into the electrolyte compartment and changing the reference electrode potential.

The measurements were conducted in Ar inert gas box with a O_2(g) meter reading less than 1ppm and constant temperature of 25°C.

Approximately 15mL of each sample was contained in a 20mL vessel and the solution was continuously stirred. A small magnetic stirrer bar was used (1cm long and 2mm of diameter) in order to minimise the effect of transport in and out of the electrode surface as well as colloids effects that could clog the electrode membrane.

Before contacting the electrode with the sample, it was gently rinsed with MilliQ water and dried with tissue paper. The combined electrode was kept into an electrolyte solution when not in use.

Redox potential data of most of the samples were read from 1 minute up to 1hour, however, in order to check the performance of the electrode over long periods of time, in some samples the electrode was left measuring over night. Following these long measuring times, no obvious leakage of external electrolyte was observed.

The metallic surface of the electrode was cleaned using a tissue paper with toothpaste at the beginning and almost at the end of the exercise and the Eh of two buffer solutions (+ 220 mV and +236 mV; at 25 °C) was periodically checked..

Solutions measured

Table 1 indicates the description of the measured samples together with the pH measured by PSI (Jan Tits and Xavi Gaona).

Sample Reference	pH (determined by PSI)	Description
REF1 Fea	8.6	100mg/L Fe-powder, pH not fixed (. 9)
REF1 Feb	6.9	100mg/L Fe-powder, pH 5-6 fixed with MES buffer
REF1 (II/III)a	5.2	$FeCl_2$,$FeCl_3$ 1:1 buffer, 10^{-4}M each, pH 5-6 fixed with MES
REF sus. magn. a	5.4	Magnetite suspension (3.1 g/L) in 0.1M NaCl, pH 6 (1mL 1M HCl)
REF sus. magn. b	7.7	Magnetite suspension (3.1 g/L) in 0.1M NaCl, pH 8 (0.19 mL 0.1M HCl)
REF sus. mack. b	8.3	Mackinawite suspension (1.4 g/L) in 0.1M NaCl, pH 6 (0.28 mL HCl 1M)
REF2 Na b	10.8	$FeCl_2$,$FeCl_3$, 5M NaCl, 10^{-4} M (Fe(II) + 10^{-4} M Fe(III) , pH 12, fixed with NaOH
REF2 Ca b	9.9	$FeCl_2$,$FeCl_3$, 2M CaCl, 10^{-4} M (Fe(II) + 10^{-4} M Fe(III) , pH 12, fixed with $Ca(OH)_2$ (s)
REF3 ISeb	5.3	Anqui:Anhqui (3:1), total 1.6E^{-3} M reduced by Na-dith., pH 5-6 fixed with MES, + 10^{-4} M NaI
REF4 ACW1	13.3	[Ca] = 1E^{-4} M; [Si] = 1E^{-2} M; [Na] = 0.11 M; [k] = 0.18 M
REF4 ACW2	13.3	[Ca] = 1E^{-2} M; [Si] = 1E^{52} M; [Na] = 0.11 M; [k] = 0.18 M
NAT1a	8.5	Gorleben groundwater, dilute, very much humics
NAT1b	7.1	Gorleben groundwater, saline
NAT2	7.9	Sample with COX characteristics
NAT3	9.3	Sample with Grimsel characteristics
NAT4	0.6	Magnesium rich high salinity brine, (IP21 solution), 10% dilution factor

Table 1. Description of the measured samples

Expected outcome

Prior to the study, it was expected to obtain steady measurements with a tolerance of 1 mV/min drift after 20-30 minutes of measure for the reference samples and a greater drift of the redox potential when measuring natural samples, specially with the samples containing colloids which could clog the liquid junction membrane.

Outcome of the study

In Table 2 we show all the measured solutions in the same order as they were analysed together with the measurements of the buffer solution and cleaning of the metallic surface of the electrode.

Data	Measured Sample/ Operation	Eh (mV) corrected with Ag/AgCl potential (205 mV at 25C)								
		1 min	2 min	4 min	13 min	25 min	35 min	45 min		
1 _17No	REF1 Fea	88	75	36	-200	-177	-199	-218	-230 (at 50 min)	-295 (at 3h)
2_17No	Cleaning of the metallic electrode surface using tissue paper with toothpaste									
3_17No	REF1 Fea	-172	-200	-236	-289	-327	-337	-357	-367(at 50 min)	-395 (at 1h)
4_17No	REF sus. magna	-192	-116	-23	55	58	55	53	46 (at 85 min)	-
5_17No	REF sus. magnb	-127	-195	-243	-262	-268	-269	-269	-	-
6_18No	REF2 Nab	155	130	114	89	73	69	68	66 (at 1h)	-
7_18No	REF2 Cab	100	89	80	70	74	79	84	93 (at 1h)	-
8_18No	REF3 ISeb	-58	-58	-58	-58	-58	-58			
9_18No	REF4 ACW2	-675	-730	-746	-760	-767	-769	-775	-	-
10_18No	NAT1a	27	50	65	59	41	32	28	27 (at 1h)	-
11_18No	NAT3	-20	-15	-8	16	21	10	-5	-30	-65 (at 16h) -64 (at 16.5h)
12_19No	NAT1b	67	-	70	84	85	82	-	-	-
13_19No	NAT1a	85	75	67	58	54	-	-	-	-
14_19No	Buffer (+220mV at 25C)	218								
15_19No	Buffer (+236mV at 25C)	235								
16_19No	NAT2	324	304	285	237	108	73	93	99	100 (at 16h) 95 (at 16.5h)
17_19No	NAT4	560	604	640	659	-	664	-	665 (at 1h)	666 (at 1.5h)
18_19No	REF1 Fea	-248	-283	-291	-297	-301	-324	-337	-344 (at	-

									1.2h)	
19_19No	Cleaning of the metallic electrode surface using tissue paper with toothpaste									
20_19No	REF1 Fea	-232	-	-249	-269	-293	-305	-	-320 (at 1.2h)	
21_19No	REF4 ACW1	-696	-704	-715	-736	-755	-	-	-	-
22_19No	Mackeawite b	-376	-353	-330	-321	-	-	-	-	-
23_19No	REF1 Feb	-147	-186	-264	-355	-	-	-	-	-283 (at 1.6h)
24_19No	REF1 (II/III)a	290	293	289	301	281	-	-	-	-

Table 2. Measured Eh (mV) values for each analysed sample

The Eh data indicate that the electrode is not significantly affected by the memory of the electrode from the previous measurement. For instance, sample REF ISeb and REF4 ACW2 were analysed one after the other and the measured Eh was -58 and -675 mV (after 1 minute), respectively (see Figure 1).

The plot of the redox measurements of samples containing iron (see Figure 2) shown that the measuring times needed for a steady measurement are very dependant on the sample. Redox potential measurements of strongly buffered samples containing the redox pair Fe(II)/Fe(III) reach a steady potential after 13-35 minutes. However, the samples containing only Fe powder (REF1 Fea and REF1 Feb), show a continuous drift and even after 1h of measuring time there is a significant negative slope and this trend in maintained even after cleaning the metallic surface of the electrode.

Interestingly, the natural samples analysed gave steady Eh readings after 13 or 25 minutes (see Figure 3).

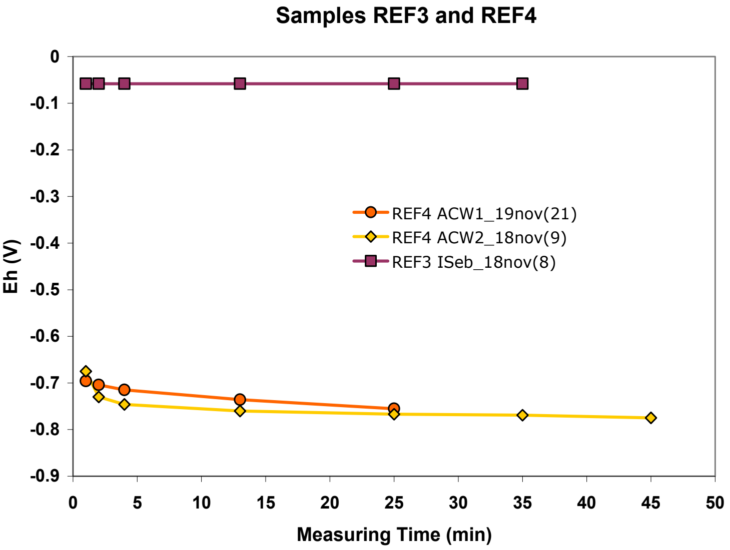


Figure 1. Measured Eh (mV) data for samples: REF3 ISeb, REF4 ACW1 and REF4 ACW2

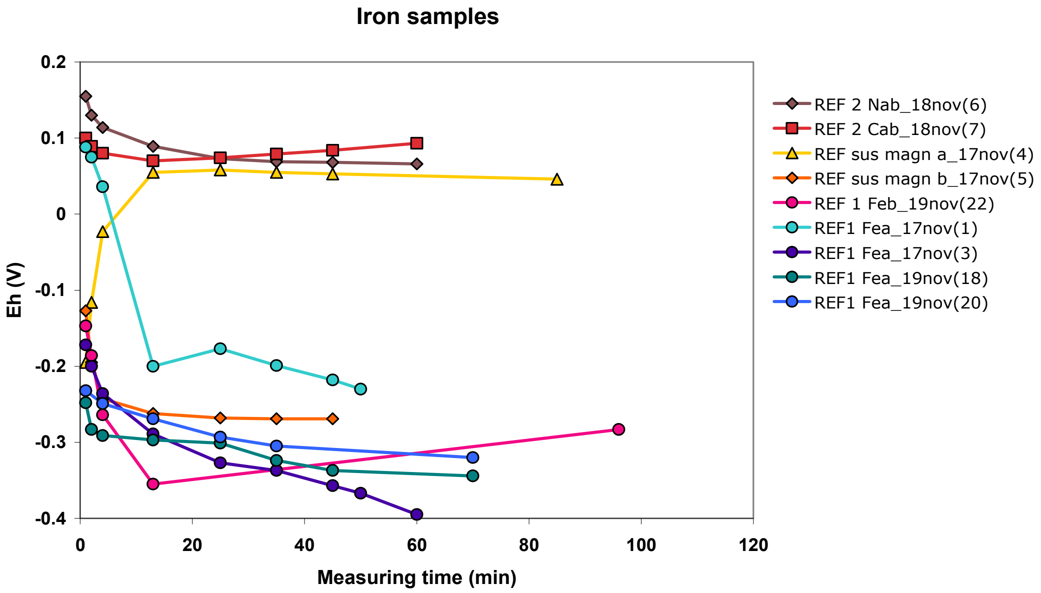


Figure 2. Measured Eh (mV) data for the iron samples.

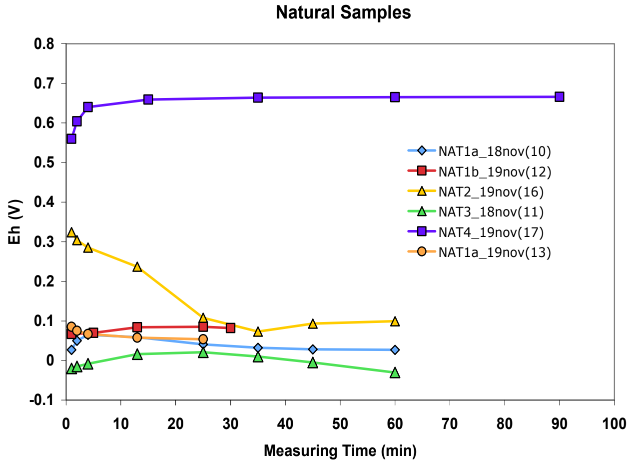


Figure 3. Measured Eh (mV) data for the anal sed anal sed natural samples

Thermodynamic approach for REF I systems

In this section the iron systems named as REF I will be discussed from a thermodynamic point of view. To this aim, it have been selected the redox measurements obtained from the different participants in Inter-Comparison Exercise using conventional combined Pt electrodes. As it has been discussed in the ICE report, the measured data have shown the importance of stirring the samples for a quicker response of the electrode. Therefore, in the current discussion only the redox measurements obtained from the samples being stirred have been chosen. Most of the participants took redox readings at different measuring times and for the present discussion, in the case of steady readings, an average value of the last measurements has been taken. For the cases with non-stable readings, it is specified in the text the way the data have been treated. For the measurements performed under 10 minutes only the cases in which the readings were significantly stable have been taken.

We have assumed $Fe(OH)_3$(am) as the most probable Fe(III) solid precipitating, according to the Ostwald's rule, for the building of the predominance pH-Eh diagrams.

Sample REF I Fe_ a and REF I Fe_b

The predominance pH-Eh diagram of iron is shown in Figure 4, where the measured Eh values for the systems REF I Fe_a and REF I Fe_b (represented as symbols) have been superimposed. The description of the studied systems is described as:

REF I Fe_a: 100 mg Fe_powder, 0.1 M NaCl, pH not fixed (9). The pH value measured by PSI was pH = 8.6

REF I Fe_b: 100 mg Fe_powder, 0.1 M NaCl, pH 5 - 6 fixed with MES buffer. The pH value measured by PSI was pH = 6.9

Despite both samples initially contained Fe(0) as the iron solid phase, the diagram shown in Figure 4 seems to indicate that the measured Eh would correspond to the thermodynamic equilibrium between aqueous Fe^{2+}/Fe_3O_4 or $Fe(OH)_2/Fe_3O_4$.

The measured redox potential of **REF I Fe_a** seems to be in agreement with the assumption of magnetite as the predominant solid phase in equilibrium with $Fe(OH)_2$ (s), In fact, the corrosion of iron by water under anaerobic conditions produces hydrogen and iron(II) hydroxide, according to the following reaction:

$Fe(s) + 2H_2O = Fe(OH)_2 (s) + H_2(g)$

$Fe(OH)_2$ (s) is metastable and with time it evolves towards the formation of a spinel-like structure oxide, exemplified by magnetite, in the so-called Schikorr reaction:

$3Fe(OH)_2$ (s) = $Fe_3O_4 + H_2 + 2 H_2O$

The composition of the magnetite formed on the surface of iron is not exactly known, although it has been suggested that it consists of an oxide $Fe_{3-x}O_4$ with a spinel-like structure varying in composition from Fe_3O_4 (magnetite), in oxygen-free solutions, to $Fe_{2.67}O_4$ under the presence of oxygen (Stumm and Morgan 1996).

The experimental data obtained from the different redox measurements are spread over a wide range of Eh (150 mV), however, the Eh readings from Amphos21 and FZD-ITU were not stable and showed a pronounced decreasing trend (represented in Figure 4 as an arrow), which might be indicative of a slow electrode response. On the other hand, Amphos21 performed two measurements of same aliquot of REF I Fe_a: before, (labelled as Amphos I) and after (labelled as Amphos II) cleaning the electrode surface with toothpaste. The results show that the cleaning the electrode surface induces a quicker response of the electrode reaching a lower Eh measurement.

Sample denoted as **REF I Fe_b**, was prepared by acidification of the aqueous suspension of Fe-powder with the addition of pH buffer. This procedure drives an increase pH and also an increase of Eh while the couple Fe_3O_4 / Fe^{+2} are in thermodynamic equilibrium. As it is shown in Figure 4, the measurements of FZD-ITU & Amphos 21 are plotted with an associated error of 50 mV in order to include the decreasing trend of the Eh readings over time.

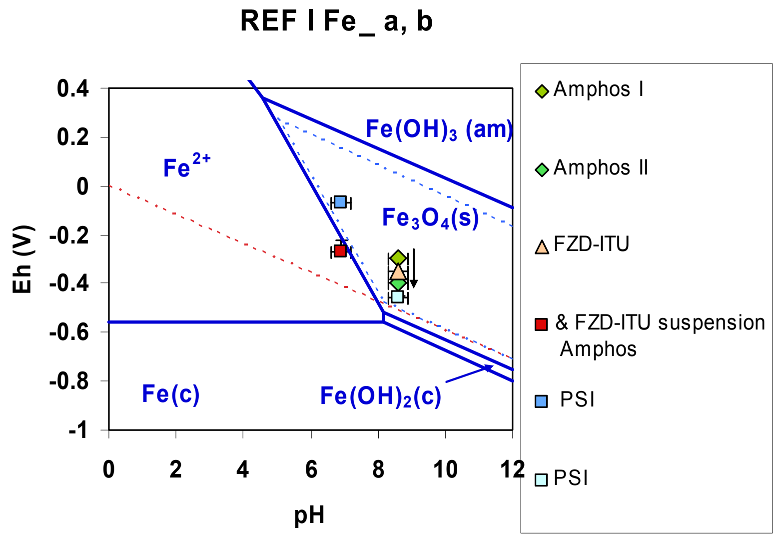


Figure 4. Predominance pH-Eh diagram of iron system. Dashed red lines accounts for the H_2O equilibrium at P = 1 atm. Dashed blue lines stand for the uncertainty associated to the thermodynamic data. [Fe] total = 0.0018 M; 0.1 M NaCl. Experimental data are represented by symbols. The error bars associated to pH correspond to 0.3 pH units.

Sample REF I Fe(II / III)_a and REF I Fe (II / III)_c

The predominance pH-Eh diagram of iron is shown in Figure 5, together with the superimposed experimental Eh values for the systems REF I Fe(II / III)_a and REF I Fe(II / III)_b (represented as symbols). The studied systems are described as:

REF I Fe(II / III)_a: $FeCl_2$ / $FeCl_3$ (1:1-buffer, 10^{-4} M each) 0.1 M NaCl, pH 5 - 6 fixed with MES. The measure pH value by PSI was pH = 5.2

REF I Fe(II / III)_b: $FeCl_2$ / $FeCl_3$ (1:4-buffer, 5.10^{-4} M total), 0.1 M NaCl, pH 2 fixed with HCl. The measure pH value was pH = 2.6.

Taking into account the uncertainty associated with Fe_3O_4 thermodynamic data (represented by dashed blue lines) the experimental measurements obtained for the system **REF I Fe(II / III)_a** seem to indicate equilibrium between Fe^{2+} and $Fe(OH)_3$(am). The Eh readings that show a certain trend with time have been represented with error bars considering an error of 50 mV towards the direction of the trend.

The four redox measurements obtained for system **REF I Fe(II / III)_b** agree with the potential of the system being controlled by the redox couple Fe^{2+} / $Fe(OH)_3$ (am).

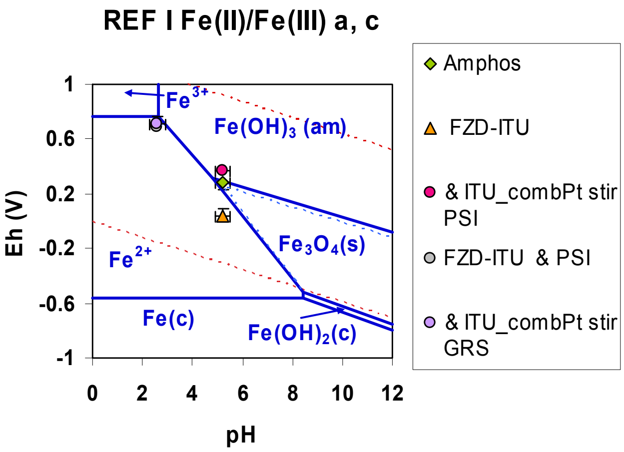


Figure 5. Thermodynamic pH-Eh diagram of Iron system (represented by solid blue lines). Dashed red lines represent the H_2O equilibrium at P = 1 atm. Dashed blue lines stand for the uncertainty associated to the thermodynamic data. [Fe] total = 5 10^{-4} M; 0.1 M NaCl. Experimental data are represented by symbols. The error bars associated to pH correspond to 0.3 pH units.

Sample REF I Sus magn_a and REF I Sus magn_b

The predominance pH-Eh diagram of iron has been plotted together with the experimental Eh values for the systems REF I sus magn_a and REF sus magn_b (represented as symbols) as shown in Figure 6. The studied systems are described as:

REF I sus magn_a: Suspension of Fe_3O_4 (0.013 M) in 0.1M NaCl, pH 6 (1 mL of 1M HCl). The measure pH value by PSI was pH = 5.4

REF I sus magn_b: Suspension of Fe_3O_4 (0.013 M) in 0.1M NaCl, pH 8 (0.19 mL of 0.1M HCl). The measure pH value by PSI was pH = 7.7

In both systems, the redox values measured by the different institutions are in very close agreement. The measured Eh values of system **REF I sus magn_a** clearly point out to a control of the redox potential by the equilibrium Fe_3O_4 / Fe^{2+}.

As for sample **REF I sus magn_b,** the representation of the experimental data on the diagram seems to indicate the redox potential is controlled by the equilibrium Fe_3O_4 / Fe^{2+}. The error bars associated to these data correspond to 0.3 pH units and account for the uncertainty related to the pH measurement of solutions with suspended particles.

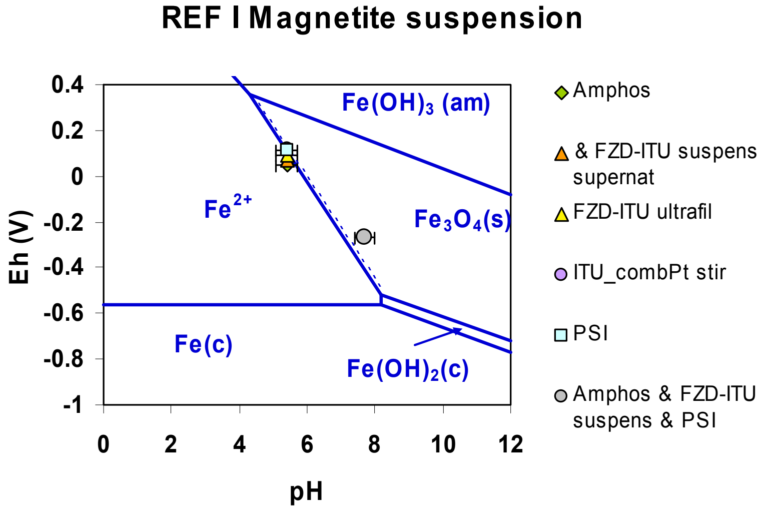


Figure 6. Predominance pH-Eh diagram of Iron system. Dashed red lines represent the H_2O equilibrium at P = 1 atm. [Fe] total = 0.001 M; 0.1 M NaCl. Dashed blue lines stand for the uncertainty associated to the thermodynamic data. Experimental data are represented by symbols. The error bars associated to pH correspond to 0.3 pH units.

Sample REF I Sus mack_a and REF I Sus mack_b

The pH-Eh diagram of iron together with the experimental Eh values for the systems REF I sus mack_a and REF sus mack_b (represented as symbols) are shown in Figure 7. The studied systems are described as:

REF I sus mack_a: Suspension of FeS (0.016 M) in 0.1M NaCl, pH 6 (*no data on the amount of HCl added*). The measure pH value by PSI was pH = 7.0

REF I sus mack_b: Suspension of FeS (0.016 M) in 0.1M NaCl, pH 8 (0.28 mL of 1M HCl). The measure pH value by PSI was pH = 8.3

The redox measurements obtained by the three partners studying this system are in very good agreement, which might indicate that the system **REF I sus mack_a** is well buffered. The diagram seems to indicate that the equilibrium FeS / Fe_3O_4 might control the Eh of the system.

In sample **REF I sus mack_b,** the pH is lower with respect to REF I sus mack_a. The diagram seems to indicate that the increase of pH has driven an increase of Eh while keeping the equilibrium between FeS(c) / Fe_3O_4(s).

ZFD-ITU obtained three different values as a function of the method used to separate the suspended particles. The data indicated a difference of 80 mV between redox potential of the suspension and the supernatant. The ultrafiltration of the sample gave place to a further increase of Eh with respect to the redox potential of the supernatant. However, we do not have the pH of the samples once they have been separated from the solid. Therefore, the representation of Eh data of the filtered solution on the pH-Eh diagrams may have associated a wide error, and thus, it has been represented with an error bar of one pH unit associated to the Eh data.

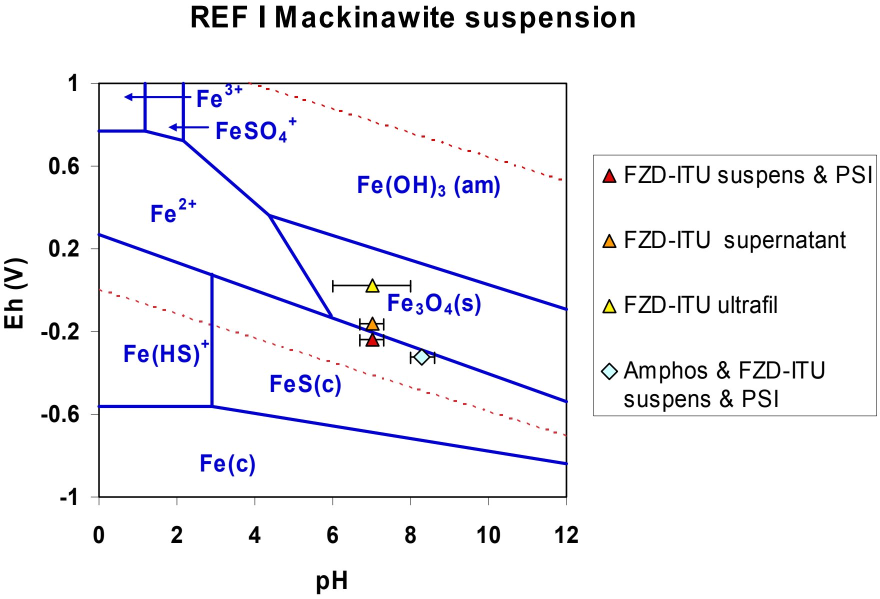


Figure 7. Thermodynamic pH-Eh diagram of Iron-Sulphur system (represented by solid blue lines). Dashed red lines represent the H_2O equilibrium at P = 1 atm. [S] total = 0.016 M; [Fe] total = 0.016 M; 0.1 M NaCl. Experimental data is represented by symbols. The error bars correspond to 0.3 pH units, except for data *FZD-ITU ultrafil* which has been taken as 1 pH unit.

Conclusions

Concerning to the response of conventional Pt electrodes over measuring time, can be extracted the following conclusions:

- It seems that conventional Pt electrodes reach quite stable readings when measuring samples from the groups: REF I, REF II. REF IV, if they are under continuous stirring. This steady state seems to be reached after pronounced drift during the first 10 - 35 minutes of measurements. This pronounced drift seems to account for the history of the electrode (a clear example is the magnetite system).

- As for the issue concerning to processes effecting the electrode such as sorption of solids on the electrode surface, there is no evidence of these processes affecting significantly the readings of reference samples, even in the case of samples with suspended particles the readings are quite stable during long measuring time (over an hour).

Concerning to the thermodynamic study of REF I systems:

- As Scott and Morgan (1999) stated, *although equilibrium approach is a poor approximation in many instances, equilibrium models are helpful in making a preliminary assessment of which redox species will interact and what the redox status will be during such interactions*. In the present exercise, we have seen that most of the studied systems could be explained by thermodynamic equilibriums among the predominant iron phases, depending on the system under study. Therefore, thermodynamic studies can be very useful in evaluating the redox potential of a system.

InterCompEx

Redox potential measurements using different electrodes and comparison with equilibrium potential computed by geochemical modelling

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Introduction

The thermodynamic equilibrium potential of the redox couples, which are present in an aqueous solution, the “Redox potential value” or E_h versus Normal Hydrogen Electrode (NHE), is generally approached by voltage measurement between an inert indicator electrode and a reference electrode. Inert indicator electrode (IIE) ideally acts as a site for reactions occurring in its local environment by functioning as a source or a sink of electrons without undergoing chemical changes itself. Therefore an IIE adopts a potential that is determined by the electron demand or availability at its vicinity with the surrounding solution [1].

In practice, however, numerous problems arise to associate the measurement a value that makes sense [2-3]. Voltage measurement problems are among the most important. Voltage measurement problems can arise due to the non-ideal behaviour of electrode materials. Platinum has been favoured as inert indicator electrode for redox potential measurements but its response also depends on its surface properties. Measurement difficulties can nevertheless be partly addressed by ensuring suitable electrode preparation (polishing, cleaning, conditioning…), and calibration before use [4].

Concerning reference electrodes, silver-silver chloride ($Ag/AgCl_{sat}/KCl$) or Saturated Calomel ($Hg/Hg_2Cl_2/KCl_{sat}$) often remain suitable for laboratory work with the appropriate maintenance.

Voltage measurement problems more frequently arise because of the nature both redox species and reactions. Species involved in irreversible and kinetically slow reactions do not participate in the redox measurement. Those involved in reversible but kinetically slow reactions are responsible for weak and unstable potential values [1,3,5]. Moreover, two or more redox equilibriums frequently occur in solution. Redox species that are not in equilibrium each other give rise to "mixed potential" measurement. It is thus rarely possible to relate the measured E_h to the activities of reduced and oxidised species present for most actual systems by a single measurement.

Within the framework of the redox observation and monitoring into the underground components of nuclear repositories, the purpose of the study was to investigate, in a semi-continuous mode of monitoring, the redox potential of reference and natural solutions via a bunch of electrodes. Each electrode response depends upon its material nature as well as its surface properties. In addition to platinum (Pt), gold (Au) and glassy carbon (GC) electrodes were investigated as inert indicator electrodes. Platinum differs from gold as it has the higher exchange current density (10 mA/cm² for Pt, against 0.3 mA/cm² for Au) [6]. However, gold is known as a more inert material: Pt is susceptible to catalyze reactions, form oxides and adsorb H_2; in contrast, gold does not. Gold has moreover a greater potential range (-0.8 to 1.8 V/NHE) towards the positive potentials (≈ 400 mV) than Pt [7].

In comparison, glassy carbon possesses a larger potential range (-1.0 to 1.0 V/NHE) towards the negative potentials (≈- 200 mV) than Au and Pt. Pure **pyrite (Py** or **FeS_2)** was selected as alterable or alternative electrode. Its interest for potentiometric measurements in bio-leaching has already been demonstrated by Cabral and Ignatiadis (2001) [8]. It was even more interesting because pyrite occurs naturally in the callovo-oxfordian (COx) formation. It was thus of a great interest to integrate it to the bunch of electrodes. For the same reasons a specific COx electrode was also designed and integrated in the bunch of electrodes for potentiometric measurements in natural COx solutions.

The test offered an advantage of great importance, because it provided information on the simultaneous behaviour of different electrodes under identical conditions. Electrode performances and robustness were examined versus time "long term measurements".

This work also aimed to:

- identify the redox reactions controlling the measured potential, both into solution and at the electrode/solution interface
- compare the obtained results with speciation measurements and geochemical modelling.

The robustness of the complementary approaches to obtain the voltage measurement it-self and its interpretation was investigated in low organic matter content samples where iron, sulphur or hydrogen redox-active species dominated redox reactions.

Experimental approach

For practical reasons (no possibility to introduce the bunch of electrodes, an electrochemical cell and a pH-meter into the Ar inert gas glove box and to connect all the electrodes to a data acquisition device), all aliquots were taken from the Ar inert gas glove box and transferred to the workbench. Transfer, that took less than one minute, was ensured in hermetically closed electrochemical cells to protect solutions from perturbation generated by atmospheric O_2 and CO_2. Electrochemical cells were placed under argon bubbling for three minutes before incorporating any electrode. Electrodes immersion was realised under argon bubbling. All measurements were then conducted under gently and continuous stirring with a magnetic stirrer and under argon atmosphere without bubbling to avoid CO_2 depletion from the samples. Despite the precaution taken during sampling and handling, aliquots could have perturbed (speciation modifications due to changes in pCO_2, and O_2 content), leading to new equilibrium conditions.

pH and temperature were followed by a SenTix 41 pH-electrode from WTW (Germany) with automatic temperature compensation.

Potentiometric measurements were performed by a 10 mm-disk shaped platinum electrode (78.54 mm²), 2 mm-disk shaped gold electrode (3.14 mm²), a 2 mm-disk shaped glassy carbon electrode (3.14 mm²) and a homemade cylindrical pyrite solid electrode (177 mm²) Each electrode was successively polished with diamond pastes (3 µm and 1 µm), rinsed with milli-Q water and dried before use. In addition, for potentiometric measurement in Nat 02 solutions, a homemade 10 mm-disk shaped COx coated platinum electrode (78.54 mm²) was used.

Potentials were measured versus Saturated Calomel Electrode (SCE), which consisted in a commercial SCE protected with a KCl 3 mol L^{-1} junction. Three SCE reference electrodes were utilised during experiments: two for the experimental analyses; the third one served as a reference in order to check the drift of the others. The two first electrodes were checked once a day versus the first one. No drift was observed over the four days of experiments. When not used, reference electrodes were stored in KCl 3 mol L^{-1}.

All indicator-electrode potentials were checked every day with a redox buffer solution (190 mV/NHE at 23.9°C). No drift was observed over the four days of experiments. Nevertheless, a problem with the use of such standards reference solutions could be their high poise. As they produce such a stable potential they are probably not capable of distinguishing between small differences in the indicator electrodes performance, such as might arise due to adsorption of chemicals onto the electrode surface or the formation of surface oxide layers. Such effects could however have influence the measured potential.

Potentiometric measurements were recorded continuously with a data acquisition system (Keithley instruments, 2700 data acquisition system) for 25 minutes at least.

PHREEQC® geochemical code was used to determine E_h and aqueous speciation by thermodynamic methods with the appropriate associated thermodynamic database (THERMODEM® thermodynamic database generated by BRGM). Redox potential calculated values were obtained from the initial conditions given by INE or from the speciation data provided later also by INE. It is worth noting that no Pitzer database was available at BRGM with regards to Fe(III). Activity coefficient correction was thus not possible. The thermodynamic calculations were not investigated for supporting electrolyte concentration higher than 0.1 mol L^{-1}.

Measured samples

Sixteen reference solutions and a natural sample were analysed, namely:
Ref 01 Fe a
Ref 01 Fe b
Ref 01 (II/III) a
Ref 01 (II/III) c
Ref Suspension Mackinawite b
Ref 02 Na a
Ref 02 Na b
Ref 02 Na c
Ref 02 Ca b
Ref 02 Ca c
Ref 02 Mg b
Ref 02 Mg c
Ref 04 MQ1
Ref 04 MQ2
Ref 04 ACW2
Ref 04 ACW1
Nat 02

Expected outcome

As the acquired potentials were measured between various inert electrodes and a common reference electrode, all electrodes immersed into the same sample, it was expected that the potential of inert electrodes would tend to a common potential value; potential stabilisation time depending upon the electrode nature and sample composition. If it was not the case, surface phenomena would be considered (adsorption, oxidation, reduction, precipitation,...).

For pyrite and COx electrodes, it was expected that one could identify the relevance of different electrochemical reactions (i.e. ionic accumulation at the vicinity of the electrode surface, in the double layer) during immersion, especially by comparison with other potential measurements obtained, in the same immersion conditions, with inert electrodes.

Finally, it was expected that continuous measurements lead to a better approach of the foreseeing redox potential, than that single measurements.

Results and discussion

Work has consisted in investigating gold, glassy carbon, pyrite and platinum electrode behaviour in low organic matter content samples where iron, sulphur or hydrogen redox-active species dominated redox reactions (figures 1 to 7).

Measured pH, temperature and potential as well as equilibration times and calculated potentials (E_h) are reported in the corresponding figure. When knew, Fe(III)/Fe(II) speciation measurement were integrated and taken into account for geochemical modelling. All potential values are expressed in Volt (V) with respect to the Normal Hydrogen Electrode (NHE). For ionic strength higher than 0.1 mol L^{-1}, pH is only given as information and is written between "!!" (limiting conditions of use of the conventional H^+-selective glass membrane).

$[Fe^{3+}]/[Fe^{2+}]$ ratios were analyzed in different supporting electrolytes (NaCl, $CaCl_2$ and $MgCl_2$) at :
- different pH (ranging from 1 to 12) and/or
- ionic strengths (supporting electrolytes concentration ranged from 0.1 to 5 mol.L^{-1}).

Figures 1, 2 and 3 present the obtained results under acidic (1), circum-neutral (2), and basic (3) conditions.

Investigations conducted in not balanced systems are shown in figures 4 and 5:
- Fe° powder immersed in pH-buffered (figure 4A) and unbuffered (figure 4B) solutions;
- Mackinawite suspension (figure 5).

The fourth set of reference samples consisting of hyper-alkaline solutions mimicking cement dissolution conditions (strongly reducing environments by addition of Na-dithionite, $Na_2S_2O_4$) are reported in figure 6.

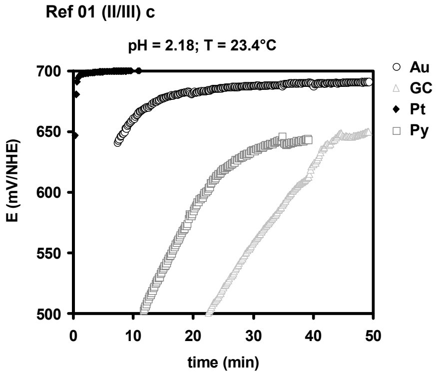
Results obtained with the natural COx clay rich rock material are presented in figure 7.

A

NaCl 0.1 mol L^{-1}
$FeCl_2$ 10^{-4} mol L^{-1}
$FeCl_3$ 4 10^{-4} mol L^{-1}
pH fixed (HCl) (2)
E_h 720mV/NHE

	[x 10^5 mol L^{-1}]*
Fe(II)	10
Fe(III)	5.59
	(mV/NHE)
E_h	705

* Provided by INE

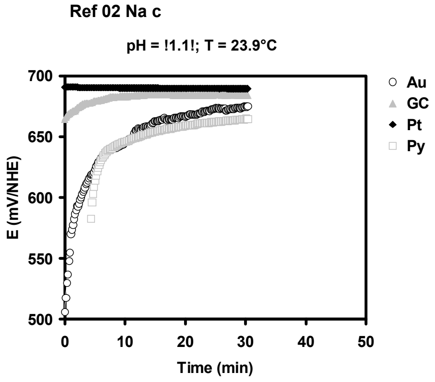

Ref 01 (II/III) c

pH = 2.18; T = 23.4°C

Electrode	Equilibration time	E (mV/NHE)
Pt	30 s	(697.0 ± 0.1)
Au	12 min	(688 ± 3)
GC	30 min	(647 ± 1)
Py	25 min	(641 ± 1)

B

NaCl 5 mol L^{-1}
$FeCl_2$ = $FeCl_3$ 10^{-4} mol L^{-1}
pH fixed (HCl) (2)

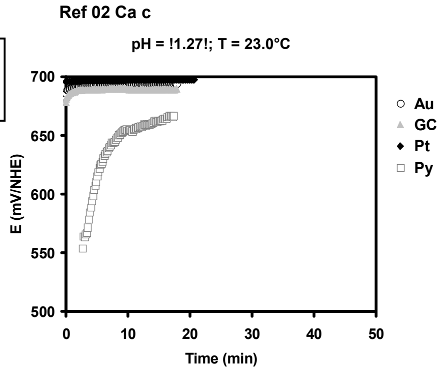

Ref 02 Na c

pH = !1.1!; T = 23.9°C

Electrode	Equilibration time	E (mV/NHE)
Pt	Instantaneous	(690.0 ± 0.4)
Au	10 min	(666 ± 8)
GC	3 min	(683 ± 2)
Py	3 min	(656 ± 7)

C

$CaCl_2$ 2 mol L^{-1}
$FeCl_2$ = $FeCl_3$ 10^{-4} mol L^{-1}
pH fixed (HCl) (2)

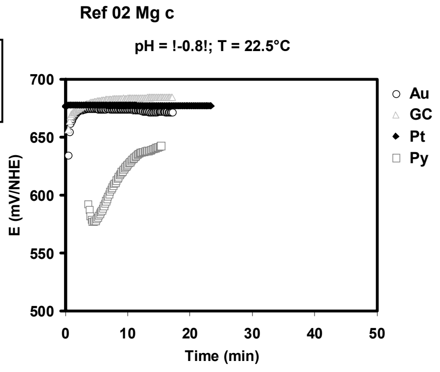

Ref 02 Ca c

pH = !1.27!; T = 23.0°C

Electrode	Equilibration time	E (mV/NHE)
Pt	Instantaneous	(696.8 ± 0.4)
Au	Instantaneous	(693 ± 2)
GC	1 min	(689 ± 1)
Py	7 min	(657 ± 7)

D

$MgCl_2$ 4.5 mol L^{-1}
$FeCl_2$ = $FeCl_3$ 10^{-4} mol L^{-1}
pH fixed (HCl) (2)


Ref 02 Mg c

pH = !-0.8!; T = 22.5°C

Electrode	Equilibration time	E (mV/NHE)
Pt	Instantaneous	(667.4 ± 0.3)
Au	2 min	(673 ± 1)
GC	4 min	(683 ± 1)
Py	9 min	(635 ± 7)

Figure 1: Results provided by the analysis of $[Fe^{3+}]/[Fe^{2+}]$ ratios under acidic conditions.

A

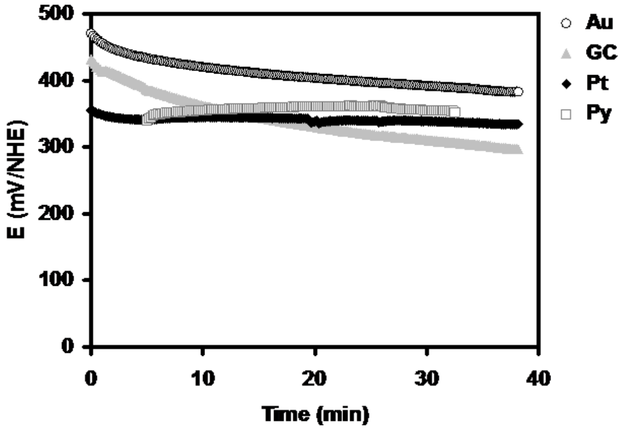
NaCl 0.1 mol L^{-1}

$FeCl_2 = FeCl_3$ 10^{-4} mol L^{-1}

pH fixed (MES) (5-6)

	[x 10^5 mol L^{-1}]*	
Fe(II)	9.39	9.55
Fe(III)	-	0.22
	(mV/NHE)	
E_h	-	492

* Provided by INE



Ref 01 (II/III) a

pH = 5.05; T = 22.7°C

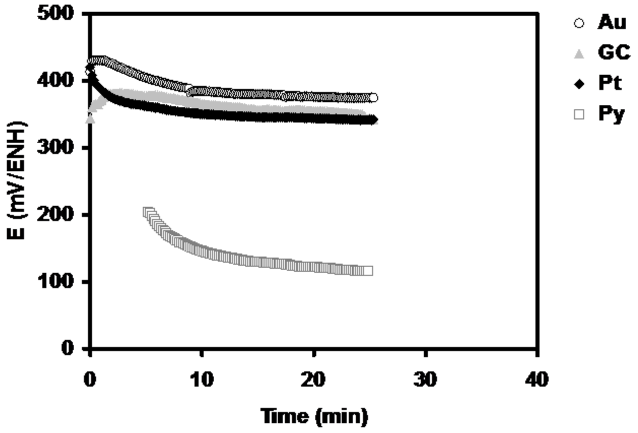
Electrode	Equilibration time	E (mV/NHE)
Pt	2 min	(341 ± 3)
Au	35 min	(384 ± 1)
GC	Unstabilized	
Py	2 min	(358 ± 3)

B

NaCl 5 mol L^{-1}

$FeCl_2 = FeCl_3$ 10^{-4} mol L^{-1}

pH fixed (HCl-NaOH) (6-7)



Ref 02 Na a

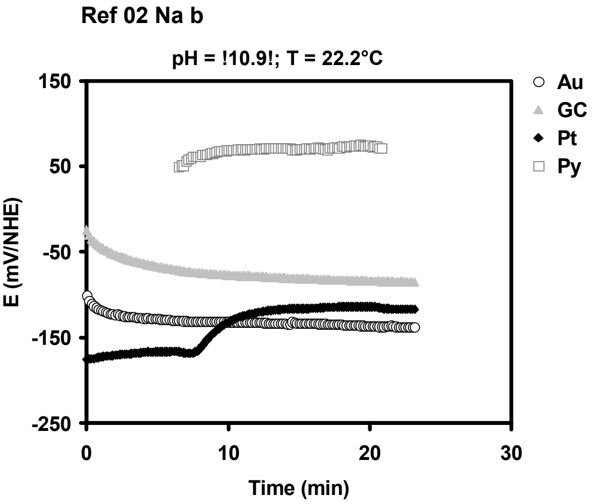
pH = !5.75!; T = 22.2°C

Electrode	Equilibration time	E (mV/NHE)
Pt	2 min	(350 ± 8)
Au	9 min	(379 ± 3)
GC	2 min	(363 ± 11)
Py	5 min	(126 ± 7)

Figure 2: Results provided by the analysis of $[Fe^{3+}]/[Fe^{2+}]$ ratios under circum-neutral conditions.

A

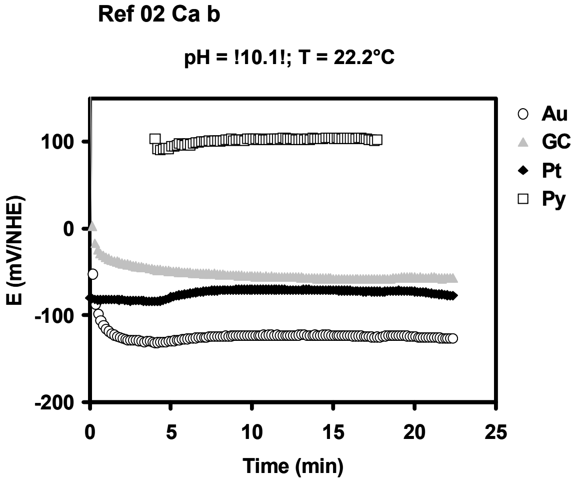
NaCl 5 mol L^{-1}
$FeCl_2$ = $FeCl_3$ 10^{-4} mol L^{-1}
pH fixed (NaOH) (12)



Electrode	Equilibration time	E (mV/NHE)
Pt	10 min	- (118 ± 4)
Au	4 min	- (133 ± 3)
GC	7 min	- (81 ± 3)
Py	3 min	- (71 ± 2)

B

$CaCl_2$ 2 mol L^{-1}
$FeCl_2$ = $FeCl_3$ 10^{-4} mol L^{-1}
pH fixed ($Ca(OH)_2$(s)) (12)



Electrode	Equilibration time	E (mV/NHE)
Pt	Instantaneous	(-75 ± 5)
Au	2 min	(-125 ± 2)
GC	4 min	(-55 ± 3)
Py	Instantaneous	(102 ± 3)

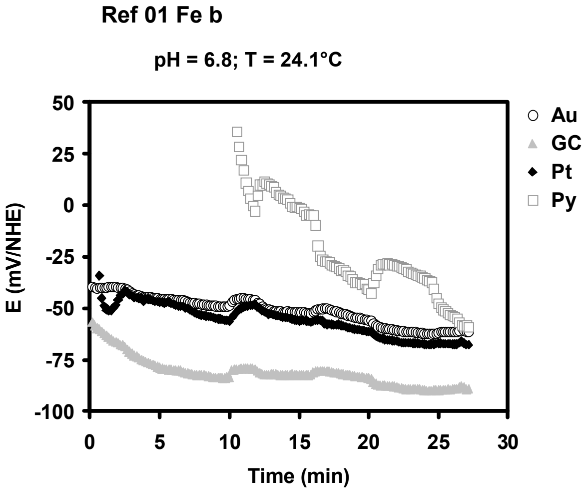
Figure 3: Results provided by the analysis of $[Fe^{3+}]/[Fe^{2+}]$ ratios under basic conditions.

A

NaCl 0.1 mol L^{-1}
Fe powder ≈ 100 mg
pH fixed (MES) (5-6)
No equilibrium

	[x 10^4 mol L^{-1}]*
Fe(II)	28.3
Fe(III)	0.168

* Provided by INE



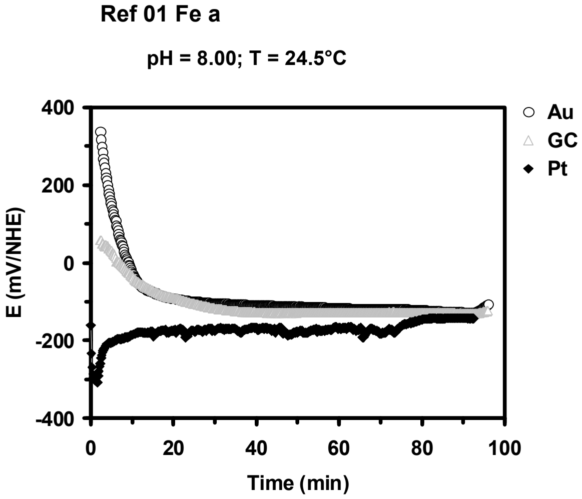
Electrode	Equilibration time	E (mV/NHE)
Pt	3 min	- (51 ± 6) - (63 ± 3) between 21 et 27 min
Au	2 min	- (52 ± 6) - (61 ± 1) between 21 et 27 min
GC	Unstabilized	
Py	15 min	- (59 ± 1)

B

NaCl 0.1 mol L^{-1}
Fe powder ≈ 100 mg
pH not fixed (≈ 9)
No equilibrium

	[x 10^6 mol L^{-1}]*
Fe(II)	2.95 ; 5.55
Fe(III)	0.3 ; 0.11

* Provided by INE



Electrode	Equilibration time	E (mV/NHE)
Pt	4 min	- (170 ± 14) - (176 ± 8) between 4 and 73 min - (149 ± 1) between 73 and 96 min
Au	15 min	- (112 ± 11)
GC	30 min	- (127 ± 3)

Figure 4: Investigations conducted in Fe° powder immersed in (A) pH-buffered and (B) unbuffered solutions.

Ref Sus Mack b

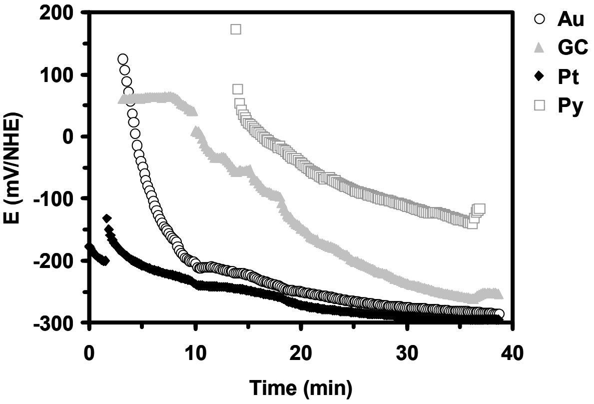
NaCl 0.1 mol L^{-1}, pH 8

Mackinawite suspension

	[x 10^6 mol L^{-1}]*
Fe(II)	2.96
Fe(III)	0.12

* Provided by INE

pH = 6.7; T = 23.3°C



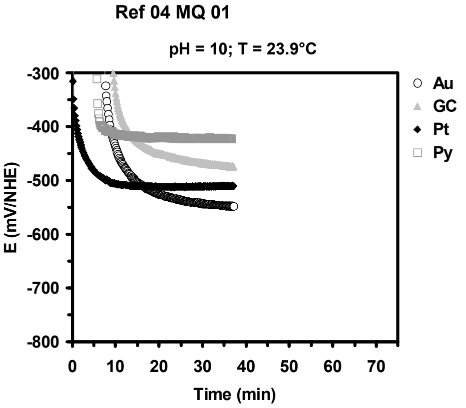
Electrode	Equilibration time	E (mV/NHE)
Pt	25 min	- (291 ± 4)
Au	25 min	- (280 ± 3)
GC	30 min	- (253 ± 2)
Py	20 min	- (271 ± 11)

Figure 5: Investigations conducted in Mackinawite suspension.

A

Ca 10^{-4} mol L^{-1}
Si 10^{-2} mol L^{-1}

[x 10^{3} mol L^{-1}]*
S(VI) 1.72
* Provided by INE

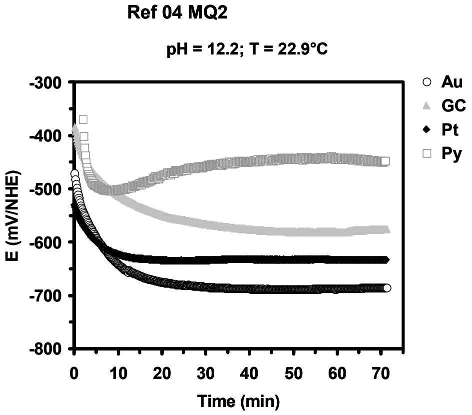


Electrode	Equilibration time	E (mV/NHE)
Pt	5 min	- (497 ± 42)
Au	13 min	- (540 ± 6)
GC	14 min	- (466 ± 6)
Py	1 min	- (418 ± 4)

B

Ca 10^{-4} mol L^{-1}
Si 10^{-2} mol L^{-1}

[x 10^{3} mol L^{-1}]*
S(VI) 2.61
* Provided by INE

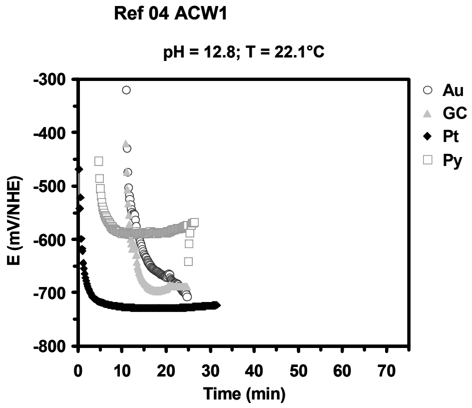


Electrode	Equilibration time	E (mV/NHE)
Pt	15 min	- (633 ± 1)
Au	25 min	- (686 ± 2)
GC	30 min	- (577 ± 4)
Py	30 min	- (446 ± 4)

C

Ca 10^{-4} mol L^{-1}
Si 10^{-2} mol L^{-1}
Na 0.11 mol L^{-1}
K 0.18 mol L^{-1}

[x 10^{3} mol L^{-1}]*
S(VI) 3.40
* Provided by INE

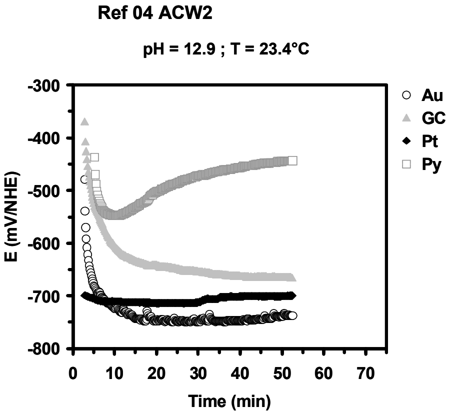


Electrode	Equilibration time	E (mV/NHE)
Pt	5 min	- (727 ± 3)
Au	Unstabilzed	
GC	6 min	- (691 ± 4)
Py	4 min	- (585 ± 8)

D

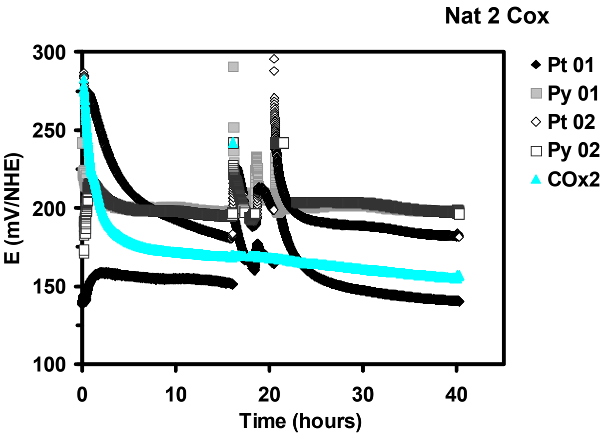
Ca 10^{-4} mol L^{-1}
Si 10^{-2} mol L^{-1}
Na 0.11 mol L^{-1}
K 0.18 mol L^{-1}

[x 10^{3} mol L^{-1}]*
S(VI) 2.94
* Provided by INE



Electrode	Equilibration time	E (mV/NHE)
Pt	5 min	- (707 ± 5)
Au	Unstabilzed	- (744 ± 4)
GC	6 min	- (657 ± 7)
Py	4 min	- (451 ± 6)

Figure 6: Redox measurement in hyper-alkaline reducing conditions obtained by sodium dithionite.



Cell 01		
t = 0	pH = 7.76	T = 23.00°C
t = 16H	pH = 8.23	T = 26.7°C
t = 20H30	pH = 8.30	T = 25.5°C
t = 40H	pH = 8.41	T = 26.2°C

Cell 02		
t = 0	pH = 7.87	T = 22.9°C
t = 16H	pH = 8.30	T = 22.9°C
t = 20H30	pH = 8.34	T = 22.6°C
t = 40H	pH = 8.38	T = 22.8°C

Perturbations encountered from 17 to 22 hours were due to pH and T measurements

	[x 10^2 mol L^{-1}]*
S(VI)	1.58

* Provided by INE

Electrode	Equilibration time	E (mV/NHE)
E Pt 01	2 hours	(150 ± 10)
E Pt 02		(189 ± 15)
E Py 01	1 hour	(200 ± 2)
E Py 02		(202 ± 2)
E COx 01	5 hours	(188 ± 5)

Figure 7: Results obtained in the Callovo-Oxfordian formation environment.

Potential stabilisation times

As expected, potential stabilisation times evolve as a function of electrode material and sample composition (Figures 1 to 7). In comparison with gold or glassy carbon electrodes, the stabilisation time of platinum electrode was constantly faster. Indeed, platinum has the higher exchange current density (10 mA/cm² in comparison to 0.3 mA/cm² for Au) [2], leading to a reasonable response time. Shorter stabilisation times (nearly instantaneous) were encountered in acidic media in which processes controlling the concentration of the redox sensitive elements are kinetically fast reactions. In samples where pH was near to neutral, a longer stabilisation time was observed (from 2 min to hours). This demonstrates the importance of the continuous monitoring of the voltage measurement for providing qualitative information on redox potential.

Influence of the supporting electrolyte (nature and concentration)

Investigations with reference to ionic strength and nature of the supporting electrolyte in thermodynamically equilibrated Fe(III)/Fe(II) samples were highly interesting (figures 1, 2 and 3). Independently of the inert electrode (Pt, Au and GC) the voltage measurement was not or little affected, whereas both the solution conductivity as well as the speciation were affected, due to the increase in salinity. This means that the term $[Fe^{3+}]/[Fe^{2+}]$ is practically unaffected. This implies that assuming the ratio of the activity coefficients, $\gamma_{Fe3+}/\ \gamma_{Fe2+}$ as equal to 1 has a minor effect on the measured redox potential.

Electrode performances and robustness

Inert electrodes

The potential acquired by all the immersed inert electrodes generally converges to a value of the same order of magnitude, independently of the sample (as illustrated in figures 1, 2, and 3 for systems in thermodynamic equilibrium, or as shown in figures 4 and 5 for systems far from thermodynamic equilibrium). This fact demonstrates that, under the same experimental conditions, the redox couples fixe identically the potential of inert electrodes (i.e. outcome of the same equilibrium state whatever the inert electrode). In the case when acquired potential did not converge, interface phenomena occurred (adsorption, oxidation, reduction, precipitation, accumulation of ions...). For example, the acquired potential of gold when immersed in very acidic samples (figure 1: Ref 02 Ca c, Ref 2 Na c, Ref 02 Mg c) illustrates some possible gold oxidation. By comparing the Au potential between the three samples, it was worth noting that increasing the activity of dissolved chloride would slightly decrease the stabilization potential of the electrode (Au-chloride complexes, $AuCl_4^-$ and $AuCl_2^-$ are more stable and more quickly formed) [6]. Organic compounds (like surfactants or humic substances encountered in natural samples) are frequently adsorbed onto carbon working surfaces. This adsorption leads to the disturbance of the redox measured potential. Adsorption phenomena onto glassy carbon electrode are significantly illustrated in figure 2A (Ref 1 (II/III)a) and in figure 4A (Ref 01 Fe b) when measurements were realised into 2-(N-morpholino)ethanesulfonic acid (MES) buffered samples. Indeed, MES is both able (i) to be adsorbed onto glassy carbon surface and (ii) to complex metallic ions. In such case, where the major part of Fe(III) was precipitated, MES adsorption on glassy carbon leads to Fe(II) pre-concentration at the electrode vicinity, thus generating progressive decrease in the Fe(III)/Fe(II) ratio at the electrode/solution interface and consequently, in the electrode potential value.

Pyrite electrode

As expected, pyrite electrode differs from the inert electrodes. In comparison with gold, glassy carbon and platinum, one can identify the relevance of different redox reactions at the vicinity of the pyrite electrode surface. The only oxidizing agents presents in the investigated samples able to oxidise pyrite were Fe^{3+} and O_2 (when samples were perturbed by atmospheric air). FeS_2 oxidation can be subdivided into the oxidation of sulphide-sulphur (first oxidation step) and the oxidation of ferrous-iron (second oxidation step; Table 1) [2].

Table 1: The different steps of pyrite oxidation including partial reactions as mobilising reactions (increase of mineralisation and possible acidification).

First oxidation step of pyrite oxidation (sulphide oxidation):

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad \text{(reaction 1)}$$

$$14Fe^{2+} + 7/2O_2 + 14H^+ \rightarrow 14Fe^{3+} + 7H_2O \qquad \text{(reaction 2)}$$

$$\text{Total} \quad FeS_2(s) + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad \text{(reaction 3)}$$

Second oxidation step of pyrite oxidation (ferrous-iron oxidation) and $Fe(OH)_3$ precipitation:

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad \text{(reaction 4)}$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \qquad \text{(reaction 5)}$$

$$\text{Total} \quad Fe^{2+} + 1/4O_2 + 2.5H_2O \rightarrow Fe(OH)_3 + 2H^+ \qquad \text{(reaction 6)}$$

Complete pyrite oxidation (sulphide and ferrous-iron oxidation):

$$FeS_2(s) + 15/4O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \qquad \text{(reaction 7)}$$

Fe^{3+}/Fe^{2+} couple has thus a decisive influence on the behaviour of pyrite electrode. That is the reason why different pyrite electrode behaviours have been observed as a function of pH:

- <u>Pyrite behaviour in acidic media ($pH \leq 2$) (figure 1)</u>: Pyrite electrode acquired a potential which was increasingly lower than that of the platinum (figure 1), which measures the redox potential of the solution. The lower value of pyrite at this pH can be explained by the interfacial pyrite oxidation (Table 1, Reaction 1), leading to the increase in Fe^{2+} at the vicinity of pyrite electrode. As the pyrite electrode has Nernstian behaviour (Cabral et Ignatiadis, 2001), the equilibrium value is decreased because the Fe^{3+}/Fe^{2+} ratio at the electrode interface is lower than that of the solution.

- <u>Pyrite behaviour at circum-neutral pH ($4.7 \leq pH \leq 7.0$) (figure 2):</u> It is important to note that, at low ionic strength (figure 2A), the potential of both pyrite and platinum electrodes were practically identical. The similar voltage measured by the two electrodes implies that the processes at the vicinity of the electrodes were the same. This result is in agreement with those already obtained by Cabral et Ignatiadis (2001), demonstrating that, in particular conditions, pyrite can act as redox electrode. These conditions can, for example, be encountered in the initial COx formation. In comparison with acidic media, at low ionic strength, pyrite oxidation/dissolution is lowered. The increase in pH diminishes the oxidizing capacity of Fe^{3+}. The redox potential is thus fixed, for the two electrodes (Pt and Py), via the $Fe(OH)_3/Fe^{2+}$ couple, which is dependent of $Fe(OH)_3$ solubility as a function of pH. High ionic strength, leads to an increase in the oxidizing capacity of Fe^{3+} versus pyrite. It thus leads to an accumulation of Fe^{2+} at the vicinity of pyrite electrode, consequently generating progressive decrease in the Fe(III)/Fe(II) ratio at the pyrite/solution interface and thus in the electrode potential.

- <u>Pyrite behaviour under alkaline conditions ($pH \approx 9$ or higher) (figure 3):</u> A higher potential value of pyrite at these pH in comparison with the potential acquired by platinum can be explained by an anoblishment process on the pyrite surface. Indeed, at higher pH than 7 iron hydroxide coagulates and stabilizes chemically to form an iron hydroxide coating at the pyrite electrode surface [9]. The combination of equation 1 and 5 (Table 1) leads to Fe^{3+} depletion in solution and in the pyrite/solution interface. $Fe(OH)_3$ coating onto the pyrite electrode responsible for the lowering of pyrite oxidation/dissolution. According to reaction 5, pyrite resulting anoblisment lead to the decrease in pH at the electrode. When the solution redox potential (Pt) is fixed by $Fe(OH)_{3(s)}/FeOH^+$ couple (with $E_{eq} = -1.14 - 0.06 \log[FeOH^+] - 0.03\log[OH^-]$), the pyrite electrode potential is fixed by $Fe(OH)_{3(s)}/Fe^{2+}$ couple (with $E_{eq} = -1.46 - 0.06 \log[Fe^{2+}] - 0.01 \log[OH^-]$).

These results confirmed, with absolute clarity, that the behaviour of pyrite is a function of the Fe(III)/Fe(II) ratio at the interface. These results are even more interesting because they lead to highlight the double interest of pyrite electrode as both redox and pH indicator when integrated in the bunch of electrodes. In fact, in natural conditions, i.e. those of initial COx formation, pyrite can operate as redox electrode (its potential is similar to that of an IIE). An increase of its potential versus the potential of an IIE can be correlated to an alkaline environment: pyrite electrode can thus behave as a pH indicator. This can be applied in the case of COx formation during its envisaged evolution as nuclear waste repository.

Comparison between measured potential, speciation measurements and geochemical modelling

It is worth noting that no Pitzer database was available at BRGM with regards to Fe(III). Activity coefficient correction was thus not possible. The thermodynamic calculations were not investigated for supporting electrolyte concentration higher than 0.1 mol L^{-1}.

$[Fe^{3+}]/[Fe^{2+}]$ ratio under acidic or circum-neutral conditions

With regards to speciation analysis, voltage measurements provided by platinum electrode were in agreement with E_h provided by geochemical modelling, particularly, under acidic conditions (figure 1A; Ref 1 (II/III)c). Concerning the circum-neutral media (figure 2A; Ref 1 (II/III)a), goethite and hematite were excluded from the predictive calculation. Ferrihydrite, $Fe(OH)_3$, was used as the relevant ferric iron hydroxide mineral. Predictive calculation with initial Fe(III) and Fe(II) contents, considering precipitation of ferrihydrite, leads to a redox potential value, E_h = 370 mV/NHE, due to Fe(III) decreasing concentration, i.e. $Fe(OH)_3$ precipitation). Speciation measurements are in good agreement with the geochemical tendency. Nevertheless, the geochemical modelling demonstrates the strong dependence of the E_h versus the Fe(III) residual concentration provided by $Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3$ (table 2). In fact, the redox potential is fixed by the $Fe(OH)_3/Fe^{2+}$ couple, which is dependent of $Fe(OH)_3$ solubility as a function of pH.

Table 2: Influence of Fe(III) residual concentration on E_h (Ref 1 (II/III)a) at pH 5.05 and constant Fe^{2+}.

Fe(II) (x 10^5) (mol L^{-1})	Fe(III) (x 10^7) (mol L^{-1})	Eh (mV/NHE)
9.39	0.50	377
9.39	0.60	342
9.39	0.80	349
9.39	1.0	355
9.39	1.5	365
9.39	1.7	368
9.39	2.0	372
9.55	22.4	492*

* Calculated using speciation measurements provided by INE

These results aimed to demonstrated that, even at trace concentration, Fe(III) plays a strong determining role on the E_h value. Near to neutral pH, any O_2 dissolution can modify the $Fe(OH)_3$ content via $2Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow 2Fe(OH)_3$. Consequently, the redox potential will increase so as to respect the solubility constant. This completely justifies the dispertion of redox potential values measured by the ICE partners (some dozen of millivolts) and also the calculated value (492 mV/NHE) using speciation measurements provided by INE.

We assume that, despite of the precaution taken during sampling and handling, aliquots can have been perturbed, leading to a novel equilibrium (in the same order of magnitude to the one expected). Nevertheless, results provided at higher ionic strength (figure 2B) are in agreement with those obtained in NaCl 0.1 mol L^{-1} (figure 2B) (sample Ref 02 Na a differs from sample Ref 01 (II/III)a by the increase in NaCl). These results demonstrated the reliability of the investigated analytical methodology :

- the reproducibility in sampling and handling

- the reproducibility via the voltage measurement provided by each type of electrode. Moreover, acquired potential voltages were generally comparable to those obtained by other ICE partners into the glove box, showing that samples were relatively well preserved during sampling, handling and measurement setup.

Fe powder under circum-neutral conditions
Some Fe° was analyzed in NaCl 0.1 mol L^{-1} at different pH (Figure 4).
There is no thermo-dynamical equilibrium between iron and H_2O. In anaerobic condition, Fe° corrodes as Fe^{2+} as follows: $Fe° + 2H^+ \rightarrow Fe^{2+} + H_{2(g)}$. At pH 8, the redox couple that fixes the potential is $H^+/H_{2(g)}$. E_{eq} is written as follows:

$$E_{eq}=0 + 0.059 \log([H^+]/pH_2) = 0 -0.059 \times 8 - 0.059 \log(\approx 10^{-3})\approx - 0.3V/NHE.$$

Consequently, the lower the measured value, the better the measurement.

In the presence of O_2, Fe° is also corroded as Fe^{2+} ($O_2 + 2Fe°+ 4H^+ \rightarrow 2Fe^{2+} + H_2O$). In addition, Fe^{2+} is oxidised as Fe^{3+}. Thus, Fe^{3+}/Fe^{2+} progressively becomes the predominant redox couple leading to the progressive increase of the redox potential. The O_2 disturbance can explain the dispertion of redox potential values measured by the ICE partners. The presence of dissolved Fe(III) (provided by speciation measurements: Fe(III): 3 10^{-7} mol L^{-1}, Fe(II) 2.95 10^{-6} mol L^{-1}) corroborates the presence of oxygen. In all cases, there is enough OH^- available for further Fe^{3+} precipitation.

The convergence to a stabilized potential (figure 4A; Ref 01 Fe b and figure 4B; Ref 01 Fe a) demonstrates the limitation of the O_2 intrusion (absence of total oxidation). Considering the disturbance by atmospheric O_2 in sample Ref 01 Fe a, the geochemical modelling predicts :

- E_h = -165 mV/NHE in the presence of lepidocrocite + 0.1 10^{-6} mol L^{-1} Fe(II) in solution.
- E_h = -157 mV/NHE in the presence of Goethite + 0.07 10^{-6} mol L^{-1} Fe(II) in solution.

Nevertheless, problems of solubility uncertainties are assumed in the database.

This example highlights that for oxygen sensitive not well balanced systems, speciation should absolutely be preserved to provide qualitative information about redox conditions. Nevertheless, preserving initial conditions is extremely difficult. A complementary approach consists in investigating solution speciation and solid analysis for redox determination by geochemical modelling in order to reliably compare it to the electrode voltage measurement and finally understand possible sample evolution.

Redox measurement in hyper-alkaline reducing conditions obtained by sodium dithionite

The fourth set of references consisting of hyper alkaline solutions obtained by sodium dithionite were realized with different concentration of silica (Figure 6). At the investigated pH domain the dissolved silica (as $H_3SiO_4^-$ and $H_2SiO_4^{2-}$) concentration is very high. Thus, dissolved silica participated to pH fixation. Sodium dithionite in solution is very unstable, decomposing thermally and oxidatively into sulphite and sulphate. These reactions are OH^- consuming.

In the absence of oxygen, the thermal decomposition is as follows:
$Na_2S_2O_4 + 2NaOH \rightarrow 2Na_2S_2O_3 + 2Na_2SO_3 + H_2O$ Reaction 8:
$3Na_2S_2O_4 + 6NaOH \rightarrow Na_2S + 5Na_2SO_3 + 3H_2O$ Reaction 9:

In the presence of oxygen, the oxidative decomposition is as follows:

Reaction 10: $Na_2S_2O_4 + O_2 + 2NaOH \rightarrow Na_2SO_4 + Na_2SO_3 + H_2O$

Considering only the thermal decomposition (reactions 8 and 9), the redox couples that can fixe the redox potential are:

$S_2O_4^{2-}/S_2O_3^{2-}$; with $E_{eq}(V) = 0.826 - 0.0591\ pH$ at 25°C
$SO_3^{2-}/S_2O_4^{2-}$; with $E_{eq}(V) = 0.526 - 0.1182\ pH + 0.0295 \log(c)$ at 25°C
$S_2O_4^{2-}/S^{2-}$; with $E_{eq}(V) = 0.170 - 0.0473\ pH + 0.0054 \log(c)$ at 25°C

Where c is the total sulphur concentration.

Considering only the oxidative decomposition (reaction 10), the redox couples that can fixe the redox potential are :

$SO_3^{2-}/S_2O_4^{2-}$; with $E_{eq}(V) = 0.526 - 0.1182\ pH + 0.0295 \log(c)$ at 25°C
SO_4^{2-}/SO_3^{2-}; with $E_{eq}(V) = -0.107 - 0.0591\ pH$ at 25°C

Where c is the total sulphur concentration

As can be seen by the E_{eq} equations, pH is a strongly influent parameter versus the redox potential.

Investigations, conducted by geochemical modelling using the above redox couples and reactions, established that the couples able to fix the redox potential are: $SO_3^{2-}/S_2O_4^{2-}$ and SO_4^{2-}/SO_3^{2-}. More precisely, the most suitable is the mixed couple $SO_4^{2-}/S_2O_4^{2-}$ with:

$$E_{eq}(V) = 0.312 - 0.079\ pH + 0.010 \log([SO_4^{2-}]^2_{eq}/[S_2O_4^{2-}]_{eq}) \text{ at } 25°C.$$

This means that initial dithionite was both thermally decomposed and chemically oxidised. This suggestion is corroborated by sulphate content analysis in the final solution. The inert electrodes voltage measurement is in excellent agreement with the geochemical modelling.

Concerning pyrite electrode behaviour in such a sample, pyrite electrode potential always remains higher than that of the inert electrodes. According to Eh-pH diagrams for Geochemistry [6], dithionite reduces S° as S^{2-}. However, S° is present on pyrite FeS_2 surface (even if pyrite surface oxidised or not). The particular behaviour of pyrite is thus explained by the presence at the vicinity of the electrode surface of the $S_2O_4^{2-}/S^{2-}$ or SO_4^{2-}/S^{2-} redox couples, which equilibrium potential are written as follows:

- $E_{eq}\ S_2O_4^{2-}/S^{2-}\ (V) = 0.170 - 0.0473\ pH + 0.0054 \log(c)$ at 25°C;
- $E_{eq}\ SO_4^{2-}/S^{2-}\ (V) = 0.146 - 0.0591\ pH$,

Where c is the total sulphur concentration.

As can be seen, pH is the most influent parameter with regards to E_{eq}; i.e. the total concentration at the pyrite interface is negligible. Investigations conducted with the above equations in comparison with the pyrite voltage measurements demonstrated that both $S_2O_4^{2-}/S^{2-}$ or SO_4^{2-}/S^{2-} redox couples were responsible for pyrite electrode potential.

Redox measurement in COx formation environment

Investigation conducted into Nat 2 COx were duplicated. Two aliquots of Nat 2 were simultaneously analysed into two different electrochemical cells. Platinum and pyrite electrodes were immersed into each cell. The COx coated Pt electrode was only immersed into cell 2. Results obtained with the natural COx clay rich rock material are presented in figure 6. It is worth noting that perturbations encountered from 17 to 22 hours were due to immersion of temperature and pH electrodes for single corresponding measurements in the

holes where were fixed Pt and Py electrodes. COx coated Pt electrode has never been perturbed by any cell aperture.
It is worth highlighting the remarkable voltage measurements reproducibility between the two cells, particularly with regards to measurements provided by pyrite electrodes. Its is more interesting to note that voltage measurement tend to a convergence potential near to (190, 200 mV/NHE), even after the electrochemical cells aperture. Results are not in agreement with those provided by literature (~ -180 mV/NHE, pH~7, T~25°C) [10], in which the S(VI)/S(-II) system is assumed to fix the redox potential with the hypothetic equilibrium between pyrite and COx pore water as in the reaction 3. Nevertheless, research is in progress and scientist tend to elaborate novel methodologies to appreciate redox phenomena in COx formation. Taking into account the state of knowledge it is difficult to draw any conclusion concerning the voltage measurement. Today, investigation is in progress to determine the relevant elements that should be analysed (for speciation measurement) to give an appreciation of redox phenomena in COx formation. In reference to previous discussion, we can assume to have investigated an oxidised sample.

Conclusions

While limitations to the interpretation of E_h remain, the interest in continuous monitoring of voltage measurements using multiple redox electrodes have clearly been demonstrated in order to ensure reliable qualitative measurement.

Beyond the database reliability for low ionic strength, results demonstrated the interest in speciation measurements and confirmed the robustness of platinum as indicator electrode for redox potential value determination into solution. As expected and as other wise stated, voltage measurements supplied by gold and glassy carbon electrodes tended towards those provided by platinum (same magnitude order); demonstrating the analytical feasibility of the redox measurement via other inert electrodes. It is worth reminding that gold electrode longer stabilisation potential is due to the slower electronic exchange. Gold and glassy carbon reference electrode should also be considered for redox measurements in nuclear repositories.

Pyrite electrode behaves differently that an IIE in acidic and alkaline environments. Pyrite integration in the bunch of electrodes takes, thus, all its interest, since pyrite can indicate the pH of the solution, when its potential is compared with that of an IIE. Such a bunch of electrodes could be applied in the case of COx formation monitoring during its envisaged evolution as nuclear waste repository.

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ReCosy, Intercomparison Exercise

Within Workpackage 2 “Development of redox determination methods”

Final Report

CNRS-LCPME (16): Application of the potentiometric and the amperometric methods for the redox potential determination

Michel Perdicakis and Carine Streiff

Introduction

Potentiometry is one of the most popular, if not the most popular, electrochemical technique. It is used daily by millions of people around the world and constitutes for many of them the only known 'electrochemical' technique. Because of its extreme versatility and ease of implementation, potentiometry is used worldwide by a broad range of scientists and engineers, from chemists to biologists to geologists for extremely different purposes. As long as the potentiometric measurements are used qualitatively for the monitoring of titrations or various repetitive processes the operating conditions have no great importance. On the other side, if the measurements are used for the determination of thermodynamic data or for prediction calculations, very often, severe precautions must be taken in terms of the samples composition.

Already in 1984 Lindberg and Runnells[1] pointed out that there were high discrepancies (as much as 1.0 V) between redox potentials directly measured in the field and those computed on the basis of individual species concentrations that have been determined by applying standard analytical methods. According to the editors of 'Redox: Fundamentals, Processes and Applications'[2], this book published in 1999 'should help to find the real value of measured redox potentials of sediments and natural waters'. However, this book, which is the sum of 15 individual contributions, presents problems rather than gives solutions but even so, among them some contributions are excellent.

During our researches for the determination of redox potentials of solutions or suspensions of minerals by the amperometric measurement of soluble electroactive species concentrations with platinum ultramicroelectrodes (UMEs), we observed that, very often, relatively large currents flow through the UME when it is maintained at the rest potential (OCP) measured beforehand at a classic platinum potentiometric electrode with a high impedance millivoltmeter ($Z > 10^{13}$ Ohm). OCP is measured with a "large" electrode than the UME to avoid the polarization of the latter. In this way, especially when electroactive species are insoluble or their concentration is very low, the difference between the OCP measured

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potentiometrically and the potential where effectively no current flows through the UME can reach few hundred millivolts.

On the other hand, experiments we performed in concentrated brines showed that UMEs prepared by sealing platinum microwires in glass as well as the commercial ones were unsuitable for voltammetric measurements in these media because of the glass corrosion that releases electroactive species, which are detected by the platinum surface. For that reason, we prepared new UMEs by sealing platinum microwires in extra-pure quartz glass (Suprasil) or by moulding them in polymer resins (epoxy or polyester).

The objective of this work is threefold. (i) Contributing to the understanding of the factors responsible for the high discrepancy observed between various potentiometric measurements in the literature. (ii) Performing a correlation between the potentiometric and the amperometric determination of redox potentials, and then, determining which of the two electrochemical techniques is the most appropriate according to the proper characteristics of a given sample. (iii) Checking the behaviour of the prepared UMEs (suprasil, epoxy or polyester) in various concentrated brines.

Experimental method and approach

The redox potential of different samples had been measured with the two techniques using the same reference electrode: a saturated calomel electrode (SCE), C10 model from Tacussel. Solutions and suspensions were both continuously stirred with a magnetic stirrer bar, unless if the suspension particles had magnetic properties themselves; in this case, the suspensions were stirred directly with the magnetic stirrer without the use of the bar. Measurements were conducted at room temperature in an argon inert gas glove box.

Classic potentiometric measurements

Apparatus: Quad pH/mV Amp (eDAQ Pty Ltd, Input impedance: $>10^{13}$ Ω, Input leakage current: $<3\times10^{-14}$ A)

Electrodes: All the measurements have been performed with a platinum rotating disc electrode (PtRDE) made of a 2.0 mm diameter platinum wire sealed in PTFE from Tacussel. Its rotation speed was 600 rpm. In certain cases, additional measurements have been made using a Pt wire (d=1 mm, h=10 mm from Tacussel) or a Pt rod (d=2 mm, h variable [30-40 mm immersed] from Metrohm).

The evolution of the potential of a platinum rotating disc electrode (PtRDE) was recorded versus the SCE as a function of time for durations that may vary according to the stability of the measured potential.

Amperometric measurements

Apparatus: 791 VA Detector, (Metrohm, Input impedance: $>10^{12}$ Ω [typ. value], Zero-point drift: 20 µV/K [typ. value], Current measurement sensitivity: 100 pA → 1 V output voltage.

Electrodes: The majority of the measurements have been performed with Tacussel MEPT 10 platinum ultramicroelectrodes (disc shaped PtUMEs, 10 µm in diameter made of platinum microwires sealed in glass). Measurements in brines have been made using home made PtUMEs constructed with 50 µm platinum wires moulded in an epoxy, or polyester, resin.

Before each measurement, both types of electrodes, PtRDE and PtUMEs, were wet-polished using abrasive sheets P#2400 and P#4000 (from Struers) then abundantly rinsed with MilliQ

<water.

Experimental procedure for the amperometric determination of redox potentials (cf. fig.1):

First step: the potential that has been previously measured potentiometrically at the PtRDE (**P0**) is applied to the PtUME through the analog potentiostat with a lower current range of 100 pA full-scale. If the current measured is null, the amperometric determination is in good agreement with the potentiometric one and the procedure stops here. If not, we proceed to the second step.

Second step: a voltammetric scan is started from **P0** in the negative direction if the current is positive (or in the positive direction if the current is negative). After, we determine the potential (**P1**) where the voltammetric curve crosses the potentials axis and the PtUME is polished again.

Third step: **P1** is applied to the PtUME and, if the current measured is null **P1** is taken as the redox potential and the procedure stops here. If not, we pass to the forth step.

Forth step: a new voltammetric scan is started from **P1** in the negative or positive direction (according to the sign of the current value) and the potential where the voltammetric curve crosses the potentials axis (**P2**) is determined and the PtUME is polished again.

Fifth step: **P2** is applied to the PtUME and, if the current measured is null **P2** is taken as the redox potential and the procedure stops here. If not, we go back to the forth step.

The forth and fifth steps are repeated until the current measured reaches the value zero.

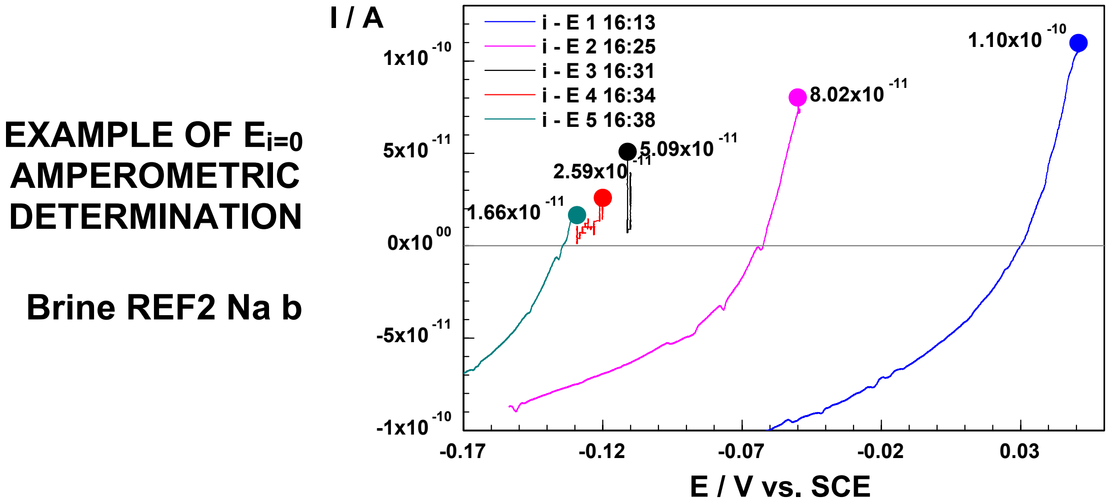


Figure 1: Schematic illustration of the experimental procedure for the amperometric determination of redox potentials.

Solutions measured

Because of technical problems encountered (cf. outcome of the study) the measurements have been carried out in two experimental runs: the first in November '09, and the second in December '09. In total, the following 14 samples have been investigated.

11/09 12/09

☐ ☒ **REF 1 Fe a**, Fe powder, 0.1 M NaCl, pH not fixed (~9)

☒ ☒ **REF 1 Fe b**, Fe powder, 0.1 M NaCl, pH 5-6 (MES buffer)

☒ ☒ **REF 1 (II/III) a**, $|FeCl_2| = |FeCl_3| = 10^{-4}$, 0.1 M NaCl, pH 5-6 (MES buffer)

☒ ☒ **REF 1 (II/III) c**, $|\mathrm{FeCl_2}| = 10^{-4}$ $|\mathrm{FeCl_3}| = 4\times10^{-4}$, 0.1 M NaCl, pH 2 (HCl)
☒ ☐ **REF 1 Sus. magn. a**, magnetite suspension, 0.1 M NaCl, pH ~ 6
☒ ☐ **REF 1 Sus. mack. a**, mackinawite suspension, 0.1 M NaCl, pH ~ 6
☒ ☒ **REF 2 Na a**, $|\mathrm{FeCl_2}| = |\mathrm{FeCl_3}| = 10^{-4}$, 5 M NaCl, pH 6-7 (titrated to pH 6-7 with HCl & NaOH)
☒ ☒ **REF 2 Na b**, $|\mathrm{FeCl_2}| = |\mathrm{FeCl_3}| = 10^{-4}$, 5 M NaCl, pH 12 (NaOH)
☒ ☐ **REF 2 Na c**, $|\mathrm{FeCl_2}| = |\mathrm{FeCl_3}| = 10^{-4}$, 5 M NaCl, pH 2 (HCl)
☐ ☒ **REF 3 HC a**, |hydroquinone|=10^{-3} M, 0.1 M NaCl, pH 5-6 (MES buffer)
☐ ☒ **REF 3 ISe a,** |hydroquinone|=10^{-3} M + 10^{-4} M NaI and $\mathrm{NaIO_3}$, 0.1 M NaCl, pH 8-9 (TRIS buffer)
☐ ☒ **REF 3 ISe b**, |anthraquinone|=1.6×10^{-3} M reduced by Na-dithionite) + 10^{-4} M NaI, 0.1 M NaCl, pH 5-6 (MES buffer). $|\mathrm{AQ}|/|\mathrm{AQH_2}|=3:1$
☒ ☒ **NAT 2**, crushed COx material equilibrated with artificial COx pore water
☐ ☒ **NAT 3**, crushed Grimsel material equilibrated with artificial Grimsel water.

Expected outcome

Prior to the measurements, we expected that:

(i) The potentials measured by the potentiometric and the amperometric techniques will be in good agreement for "redox buffered" solutions (samples **REF 1 (II/III) c** and **REF 2 Na c** [presence of relatively high amounts of soluble Fe(III) and Fe(II)] and samples **REF 3 ISe a** and **REF 3 ISe b** [where relatively high amounts of quinone and hydroquinone or anthraquinone and anthrahydroquinone are present respectively]) as well as for samples composed of dense suspensions of electroactive solids (**REF 1 Fe b**, **REF Sus magn a** and **REF Sus mack a**) if the particles size is sufficiently small, and their surface charge (zeta potential) is favourable to the covering of the platinum surface with the minerals particles.

(ii) The potentials measured amprerometrically may be quite different from those measured potentiometrically when the samples contain very low concentrations of electroactive species (**NAT 2 & NAT 3**), only one component of a redox system (**REF 3 HC a**, [hydroquinone]) or contain insoluble Fe(III) species (**REF 1 (II/III) a**, **REF 2 Na a** and **REF 2 Na b**). In these cases, potentials are extremely badly defined and the potentiometric electrodes are likely to be irreversibly polarized.

Outcome of the study

Introductory remarks

During the first run of measurements (November '09) we encountered two main electrical disturbances:

1 - A BNC coaxial adapter, allowing the electrical connexion between the inside and outside of the glove box, failed with certain BNC plugs. Therefore, we spent one day to control our equipment (potentiostat, data acquisition system, cables and electrodes) before to find the origin of the dysfunction.

2 - There was a serious problem of electrical noise inside the glove box because of the displacements of electrical charges created by the movements of the hands of other participants who worked in front of us. In these conditions, it was very difficult to measure few pico-amps; therefore, we were obliged several times to start again and again the measurements.

For that reason, in December '09 we performed a second run of measurements that has been carried out in optimum conditions, since we were the only persons in the room. During this run, we endeavoured to measure again the samples that we measured in November, if they were available, and to measure new samples.

Only PtUMEs prepared with polymer resins have been tested in brines because the prototype PtUMEs prepared by sealing platinum in Suprasil quartz glass are quite fragile (1 mm in diameter) and their handling with thin gloves turned out to be extremely delicate.

Results and discussion

Despite the unfavourable conditions for low current measurements (long cables –because the potentiostat was located outside of the glove box– and air or argon draughts by reason of the air conditioning and the stream of argon inside the box), the results, which are summarized in Table 1, are globally in good accordance with the expected ones. There are three exceptions that concern the measurements made in November '09 with the samples **REF 2 Na b**, **REF 2 Na b** and **REF 2 COX**.

In the following, we will examine one by one the results for all the samples or the groups of samples studied.

Sample **REF 1 Fe a:**

(Fe powder, 0.1 M NaCl, pH not fixed (~9))

In this case, initially, only one of the two components of the redox couple Fe(II)/Fe° is present. However, metallic iron is susceptible to react with water according to the equilibrium:

$$Fe^{\circ} + 2H_2O \leftrightarrows Fe(OH)_2 + H_2$$

The potential of the suspension is fixed by the redox system $Fe(OH)_2/Fe^{\circ}$ that depends on the pH. The pressure of gaseous hydrogen will be such that the potential given by the system H_2O/H_2 will be the same than that calculated for $Fe(OH)_2/Fe^{\circ}$. Of course, the system is in equilibrium only if the vessel is hermetically closed. However, even after the opening and closing of the vessel the equilibrium is established again, and the redox potential is the same.

Table 1: Potentials measured using the potentiometric and the amperometric method

SAMPLES	POTENTIAL DETERMINATIONS (mV/SHE)				COMMENTS
	POTENTIOMETRIC	Electrode	AMPEROMETRIC	Electrode	
REF 1 Fe a	*15/12 11:13*: **-281**$_{t=5}$ **-288**$_{t=20}$ **-191**$_{t=135\ \mathrm{min}}$	Pt RDE	*15/12 11:56*: **-327**, *15:07*: **-272**, *15:05*: **-266**	PtUME 10µm glass	
REF 1 Fe b	*18/11 13:31*: **-353** (quite stable)		*18/11 15:50*: **-350**		the mineral particles adhere to the electrodes
	15/12 16:33: **-86**$_{t=0}$ **-97**$_{t=20\ \mathrm{min}}$		*15/12 17:06*: **-97**, *17:11*: **-183**, *17:23*: **-107**, *17:24*: **-114**		
	16/12 07:25: **-151**$_{t=0}$ **-174**$_{t=20\ \mathrm{min}}$		*16/12 07:52*: **-170**, *08:16*:**-171**, *08:26*: **-166**		new sample
REF 1 (II/III) a	*18/11 09:33:* **260**$_{t=0}$ **378**$_{t=32\ \mathrm{min}}$		*18/11 10:54:* **134**		
	16/12 09:18 **32**$_{t=0}$ **83**$_{t=46\ \mathrm{min}}$ **244**$_{t=255\ \mathrm{min}}$		*16/12 10:17*: **397**, *10:43*: **350**, *10:56*: **265**, *12:33*: **335**, *14:16*: **324**		
	16/12 09:18 **16**$_{t=18}$ **186**$_{t=38}$ **321**$_{t=132}$ **321**$_{t=244\ \mathrm{min}}$	Pt wire			increase of the solid particles size: the suspension immediately settles down
	16/12 09:18 **446**$_{t=21}$ **430**$_{t=38\ \mathrm{min}}$	Pt rod			
	16/12 09:18 **-120**$_{t=259}$ **191**$_{t=271}$ **360**$_{t=287\ \mathrm{min}}$	PtRDE2			
REF 1 (II/III) c	*17/11 13:26*: **704** (quite stable)	PtRDE	*17/11 15:20*: **694***		* less sensitive potentiostat: (EG&G 174A)
	16/12 09:14 **702**$_{t=0}$ **704**$_{t=7\ \mathrm{min}}$		*16/12 14:56*: **702**, *15:04*: **702**		
REF 1 Sus magn a	*19/11 09:28:* **75**$_{t=0}$ **94**$_{t=6\ \mathrm{min}}$		*19/11 09:59:* **-116**<E<**-86**		
REF 1 Sus mack a	*18/11 16:06:* **-283**$_{t=0}$ **-237**$_{t=13\ \mathrm{min}}$		*18/11 17:02:* **-251**±5		the mineral particles adhere to the electrodes
	19/11 08:15: **-174**$_{t=0}$ **-232**$_{t=7\ \mathrm{min}}$		*19/11 08:56:*		

SAMPLES	POTENTIAL DETERMINATIONS (mV/SHE) POTENTIOMETRIC	Electrode	AMPEROMETRIC	Electrode	COMMENTS	
REF 2 Na a	*19/11 15:09:* $560_{t=0}$ $514_{t=7\ min}$	PtRDE2	*19/11 15:48:* 48	PtUME 50µm epoxy	A precipitation is observed shortly after the contact of the sample with the electrodes.	The reference electrode is inserted in an electrolyte vessel made of PCTFE with a ceramic diaphragm
	17/12 15:30: $224_{t=4}$ $232_{t=9.5}$ $236_{t=14.5}$ $258_{t=75\ min}$		*17/12 15:54*: 210, *16:48*: 164, *16:53*: 155			
	17/12 15:30: $287_{t=14.5}$ $305_{t=16.5\ min}$	Pt rod				
REF 2 Na b	*19/11 16:03:* $271_{t=0}$ $293_{t=6\ min}$	PtRDE2	*19/11 16:34*: 111			
	17/12 17:06: $180_{t=0}$ $181_{t=4}$ $171_{t=10}$ $162_{t=56min}$		*17/12 17:46*: -116, *18:14*: 3			
	17/12 17:06: $75_{t=4}$ $69_{t=6\ min}$	Pt rod				
REF 2 Na c	*19/11 13:09:* $667_{t=0}$ $699_{t=100\ min}$	PtRDE2	*19/11 14:21:* 695 epoxy *19/11 14:51:* 695 polyester	PtUME 50µm		
REF 3 HC a	*16/12 15:28*: $170_{t=0}$ $205_{t=7.7\ min}$	PtRDE	*16/12 15:45*: 247, *15:53*: 246, *16:37*: 233	PtUME 10µm glass		
REF 3 ISe a	*16/12 16:45*: $153_{t=0}$ $140_{t=7.7\ min}$		*16/12 16:59*: 118, *17:09*: 118, *18:26*: 167			
REF 3 ISe b	*17/12 08:17*: $-7_{t=0}$ $29_{t=8.3\ min}$		*17/12 08:42*: 14, *09:48*: -19, *10:15*: -52			
	17/12 10:46: -59 (quite stable)					
NAT 2 COX	*19/11 10:33:* $-298_{t=0}$ $-186_{t=20\ min}$		*19/11 11:55*: -398	PtUME 10µm glass		
	17/12 10:58: $-225_{t=0}$ $-160_{t=2.54}$ $62_{t=10}$ $119_{t=21}$ $144_{t=40}$ $171_{t=64\ min}$		*17/12 11:49*: 175, *13:09*: 130, *13:10*: 127			
	17/12 10:58: $-8_{t=2.5}$ $-40_{t=40\ min}$	Pt wire				
	17/12 10:58: $327_{t=5}$ $305_{t=38\ min}$	Pt rod				
NAT 3 Grimsel	*17/12 13:44 :* $-331_{t=0}$ $-105_{t=4}$ $72_{t=10}$ $58_{t=15min}$	PtRDE	*17/12 14:05*: 180, *15:02*: 224			

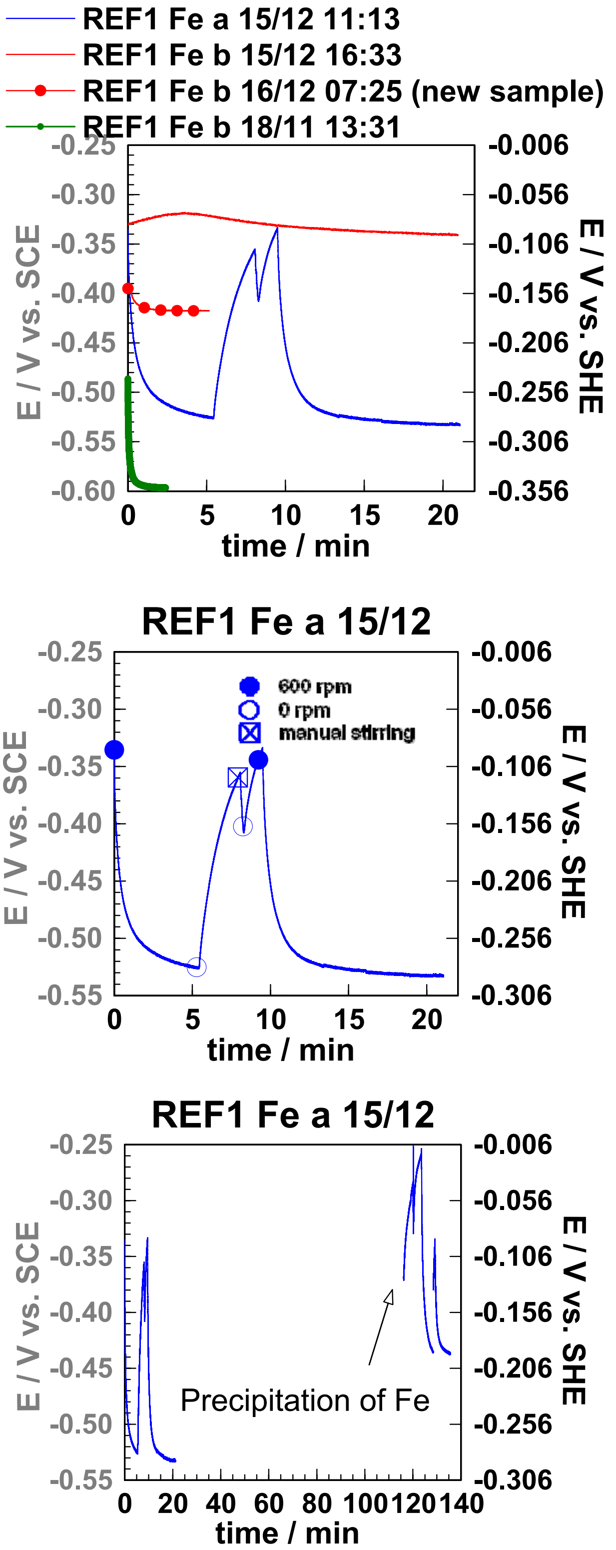


Figure 2: Potentiometric measurements performed with samples **REF 1 Fe a** and **REF 1 Fe b** at PtRDE

The fact that $Fe(OH)_2$ slowly reacts on its turn with water with the formation of green rusts (GRs): $Fe(OH)_2 + H_2O \leftrightarrows GRs + H_2$, will make the system enormously more complex (in the case of sulphated GR $E°_{Fe_6(OH)_{12}SO_4/Fe(OH)_2} = -0.56$ V vs. NHE).

The potential measured experimentally are much higher than the expected ones and the recording of the potentiometric measurements with time pointed out the extreme dependence of the potential values on the electrode rotation rate. Indeed, when the speed of rotation passes from 600 rpm to zero, the potential decreases by about 300 mV.

In any case, the potentials measured amperometrically are more negative than the potentiometric ones and when the potentiometric electrode is rotated, the difference between the amperometric and the potentiometric measurements is less than 100 mV.

Sample REF 1 Fe b:

(Fe powder, 0.1 M NaCl, pH 5-6 (MES buffer))

In these conditions, the reaction of metallic iron with water can be written as: $Fe° + 2H^+ \leftrightarrows Fe^{2+} + H_2$. If with the previous sample the loss of hydrogen had no consequences on the equilibrium potential because of the insolubility of $Fe(OH)_2$, in this case, each time when the flask is opened the loss of hydrogen is accompanied by an increase of the Fe^{2+} ions concentration that raises the redox potential. Moreover, in the measurement vessel, close to the measurement electrode, the local production of hydrogen and Fe^{2+} is a function of the amount of iron particles sampled with the liquid phase, the stirring rate and the dragging of hydrogen by the argon flow.

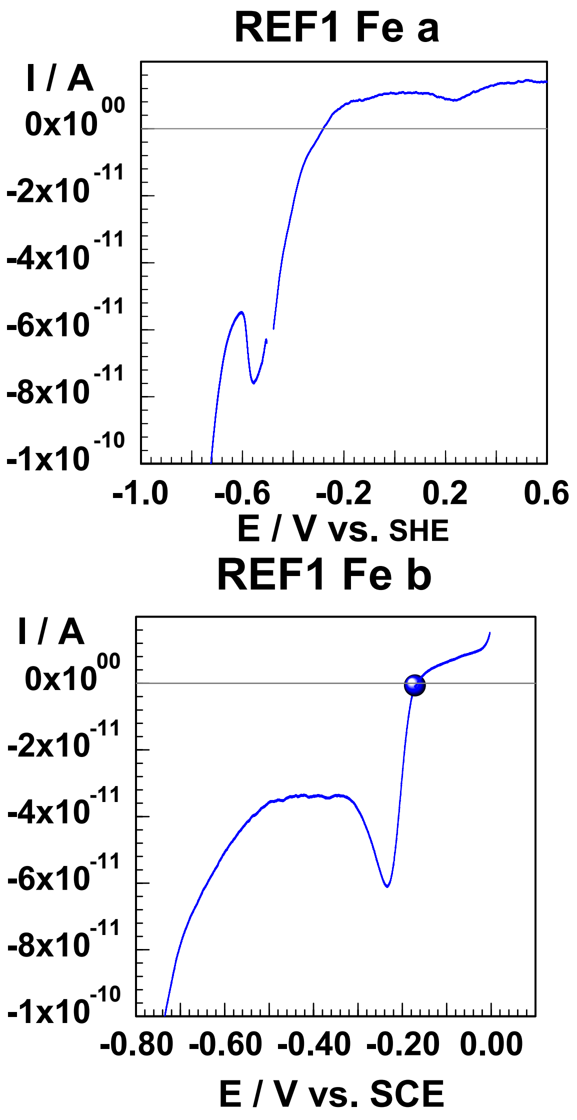


Figure 3: Voltammetric curves recorded with samples **REF 1 Fe a** and **REF 1 Fe b** at a PtUME (10 µm)

As it was expected, there is an excellent agreement between potentials measured potentiometrically and amperometrically. On the other side, because of the reasons mentioned above, one can notice a mean increase of about 250 mV between the measurements made in November and those performed in December. Anyway, all the potential measured are much higher than those thermodynamically expected.

Samples REF 1 (II/III) a and REF 1 (II/III) c:

(|$FeCl_2$| = |$FeCl_3$| = 10^{-4} M, 0.1 M NaCl, pH 5-6 (MES buffer))

(|$FeCl_2$| = 10^{-4}, |$FeCl_3$| = 4×10^{-4}, 0.1M NaCl, pH 2 (HCl))

● As with the suspension of iron **REF 1 Fe b**, where the two components of a redox couple are present, in the case of sample **REF 1 (II/III) c**, Fe(III) and Fe(II) are both soluble because of the acidic medium and the two techniques in comparison give very close potential values. These potentials are compatible with those quoted in the literature for the Fe(III)/Fe(II) system in chloride media

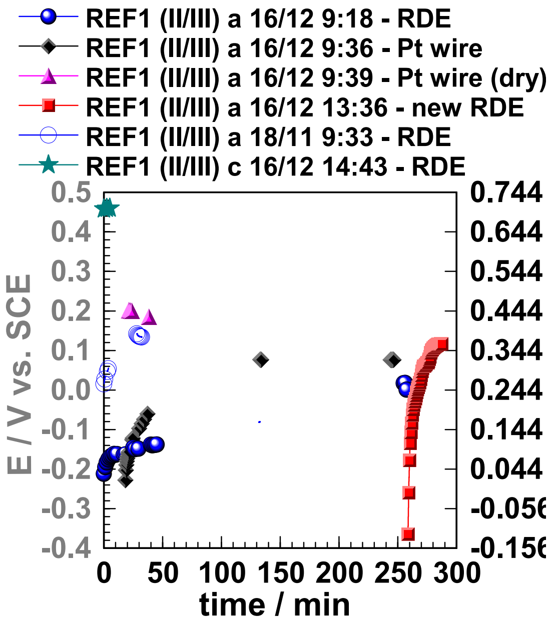


Figure 4: Potentiometric measurements performed at a PtRDE and Pt wires with samples **REF 1 (II/III) a** and **REF 1 (II/III) c**.

.However, the voltammograms recorded with the PtUME show that the limiting current for Fe(II) (~150 pA) is about two times higher than that for Fe(III) (~84 pA) that is hardly compatible with the announced chemical composition of this sample (|$FeCl_2$| = 10^{-4} M, |$FeCl_3$| = 4×10^{-4} M).

● Sample **REF 1 (II/III) a** is less acidic and Fe(III) is no more totally soluble. Moreover, one month after the first experimental run, the aspect of the sample had completely changed: the size of the solid particles had increased, and the suspension settles quasi immediately. Our impression is that the electrodes "see" only the solution and do not "see" anymore the solid particles. This is evident if we consider the potential values measured amperometrically: 134 mV vs. SHE on November '09 (which is in accordance with the Pourbaix diagram for $|Fe^{2+}| = 10^{-4}$) and about 330 mV vs. SHE on December '09.

As it was expected, on November '09 the potential determined amperometrically is much lower than that determined potentiometrically. On December '09, potentiometric measurements have been performed with four different electrodes. The results are too complex to be summarized briefly they will not be commented on here.

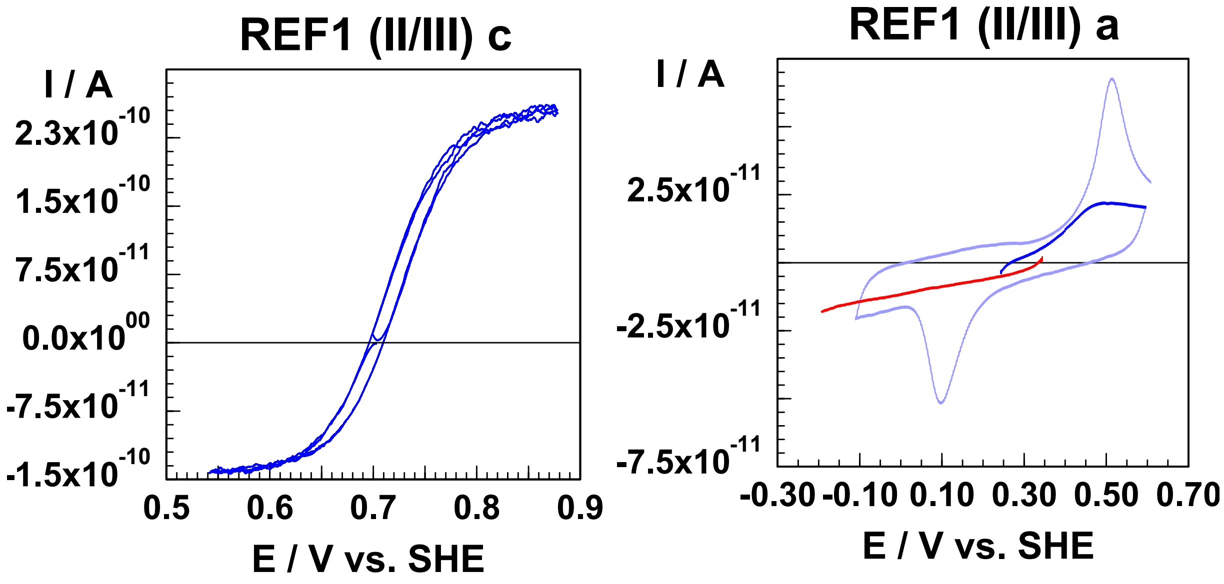


Figure 5: Voltammetric curves recorded with samples **REF 1 (II/III) a** and **REF 1 (II/III) c** at a PtUME (10 µm)

Sample REF Sus magn a:

(magnetite suspension, 0.1 M NaCl, pH ~ 6)

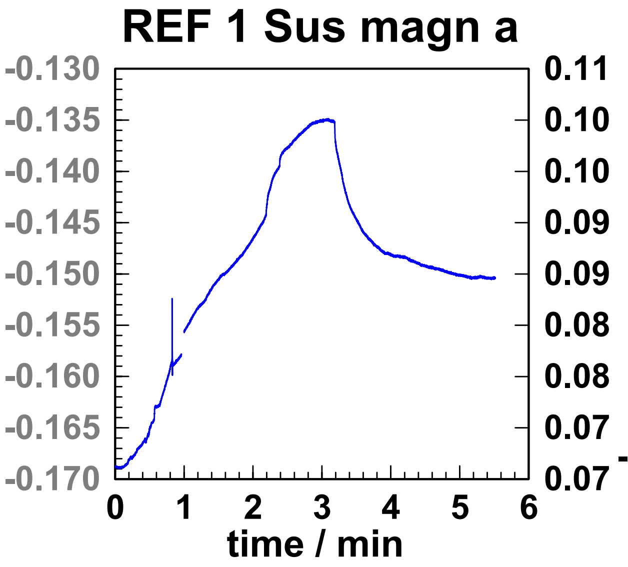


Figure 6: Potentiometric measurement performed with sample **REF Sus magn a** at a PtRDE.

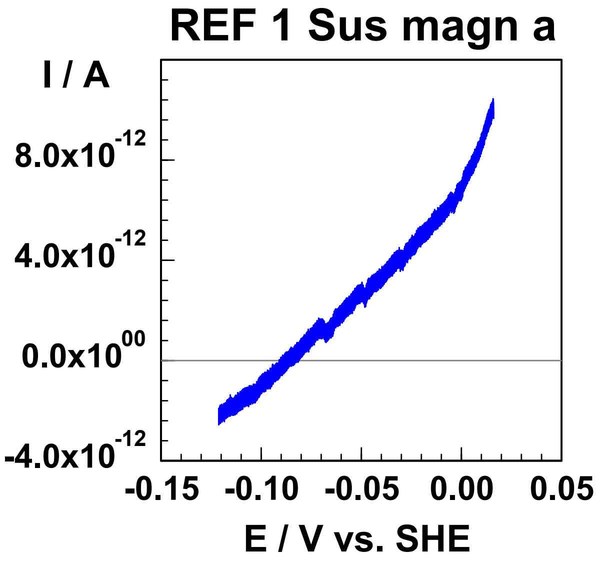


Figure 7: Voltammetric characterization of sample **REF Sus magn a** at a PtUME (10 µm)

According to the Pourbaix diagrams, at pH 6, magnetite disproportionates into Fe^{2+} and hematite according to the equilibrium: $Fe_3O_4 + 2H^+ \leftrightarrows Fe_2O_3 + Fe^{2+} + H_2O$. As the suspension is not buffered at pH 6, pH will increase, and the reaction will stop.

Depending on if hematite so formed will cover the magnetite surface or not, two redox reactions are likely to proceed at the platinum electrodes surface:

$Fe_3O_4 + 8H^+ + 2e^- \leftrightarrows 3Fe^{2+} + 4H_2O$ (I)

and/or $Fe_2O_3 + 6H^+ + 2e^- \leftrightarrows 2Fe^{2+} + 3H_2O$ (II)Moreover, if the suspension is stirred, a possible hematite layer on the magnetite surface may be seriously damaged and removed.

Anyway, as there is a certain amount of Fe^{2+} ions in the solution (resulting from the Fe_3O_4 disproportionation) if the mineral suspension adheres on the platinum surface it is expected that the potential will stable and well defined.

Contrary to that happens with the suspensions of iron powder:

- We have not observed any adhesion of the Fe_3O_4 particles to the electrodes surface
- There is a discrepancy between the potential values measured with both techniques (the potentiometric one is about 200 mV higher than that determined amperometrically).

It is very tempting to attribute the higher potential to the equilibrium (II) and the lower to the equilibrium (I) but there is a lack of sufficient experimental measurements to propose a non-speculative interpretation

Sample REF Sus mack a:

(mackinawite suspension, 0.1 M NaCl, pH ~ 6)

At pH 6, mackinawite is susceptible to react with water with production of pyrite, Fe^{2+} ions and gaseous hydrogen: $2FeS + 2H^+ \leftrightarrows FeS_2 + Fe^{2+} + H_2$.

Therefore, when we proceed to the measurements two electrochemical reactions can be involved at the surface of a platinum electrode:

$2FeS + -2e^- \rightarrow FeS_2 + Fe^{2+}$

or/and $2FeS_2 + -2e^- \rightarrow Fe^{2+} + 2S°$

(or oxidation of pyrite into other sulphur species) As the suspension is not buffered at pH 6, the pH may increase and additional reactions may intervene:

$2FeS + 2H_2O \leftrightarrows FeS_2 + Fe(OH)_2 + H_2$

$Fe(OH)_2 + H_2O \leftrightarrows GR + H_2$

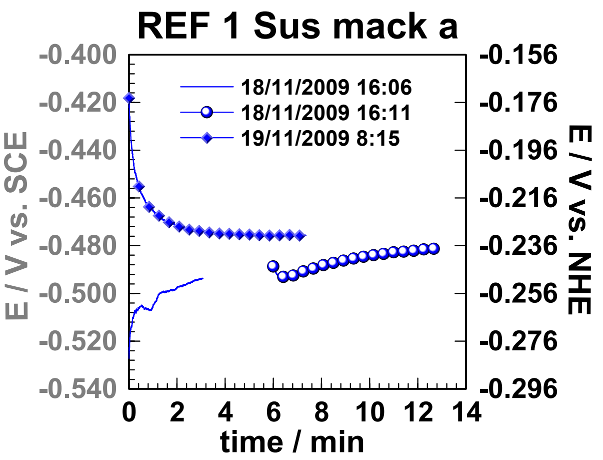


Figure 8: Potentiometric measurements performed with sample **REF Sus mack a** at a PtRDE.

The redox potential values measured potentiometrically (-235 mV vs. SHE) or amperometrically (-251 mV vs. SHE) are very close. This is probably due to the complete adhesion of the mineral in all the parts of the electrodes –the insulating ones comprised– that become completely black. The potential value of about -250 mV is quite high with respect to those that can be predicted from Pourbaix diagrams for the $FeS \rightarrow FeS_2$ transition.

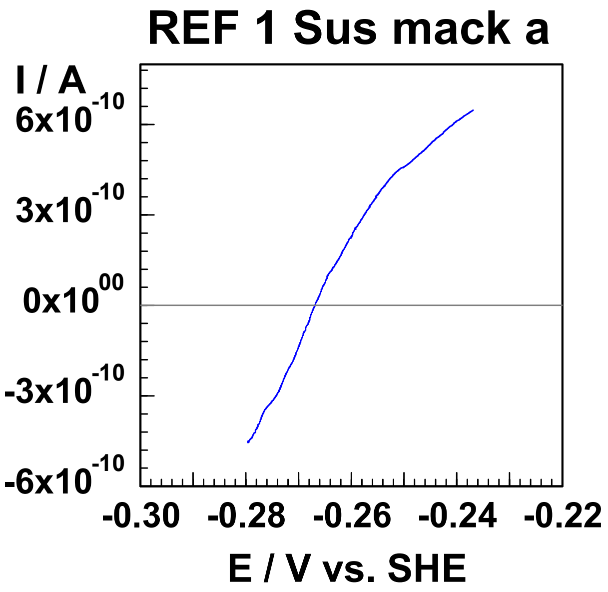


Figure 9: Voltammetric characterization of sample **REF Sus mack** at a a PtUME (10 µm)

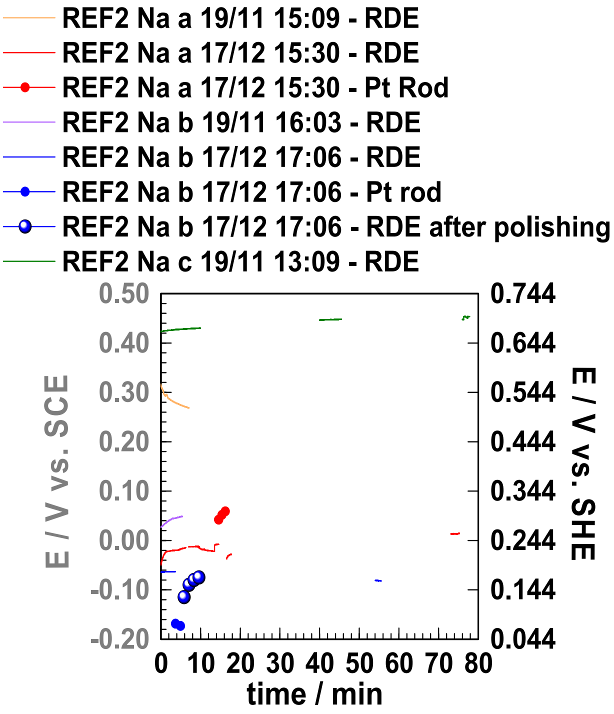


Figure 10: Potentiometric measurements performed with samples **REF 2 Na a, REF 2 Na b** and **REF 2 Na c** at a PtRDE and a Pt rod..

Samples REF 2 Na a, REF 2 Na b and REF 2 Na c:

($|FeCl_2| = |FeCl_3| = 10^{-4}$ M, 5 M NaCl, pH 6-7 (titrated to pH 6-7 with HCl & NaOH))
($|FeCl_2| = |FeCl_3| = 10^{-4}$ M, 5 M NaCl, pH 12 (NaOH))
($|FeCl_2| = |FeCl_3| = 10^{-4}$ M, 5 M NaCl, pH 2 (HCl))

General remark: concentrated brines must be considered as independent solvents. Solvations of anions and cations are quite different from those in water and the use of an extrathermodynamic hypothesis (or the knowledge of the 'water activity' of the brines) is required for the calculation of thermodynamic data, as stability constants and redox potentials, using values established in water.

● Sample **REF 2 Na c**, which contains a mixture of soluble Fe(III) and Fe(II), gives similar results as those for sample **REF 1 (II/III) c**. The two techniques in comparison give virtually the same result (amperometry 695 mV vs. SHE and potentiometry about 699).

The voltammograms recorded showed that the limiting current for Fe(II) (856 pA) is 1.25 times higher than that for Fe(III) (682 pA) although $|Fe(III)| = |Fe(II)| = 10^{-4}$ M.

With this sample, we also examined the influence of the convection on potentiometric measurements involving soluble species with rapid electrochemical kinetics. When the rotation speed of the PtRDE passes from 600 rpm to 0 the potential progressively diminishes by about 5 mV (458→453 mV) after 2 min and if the rotation starts again it recovers immediately its initial value.

In order to have a better understanding of what happens at the electrode surface during the potential measurement when the convection changes, we formulated two hypotheses by assuming that this potential decrease is in direct relationship with the modification of the amount of electroactive species that reaches or leaves the electrode surface. This aspect is developed in Appendix A.

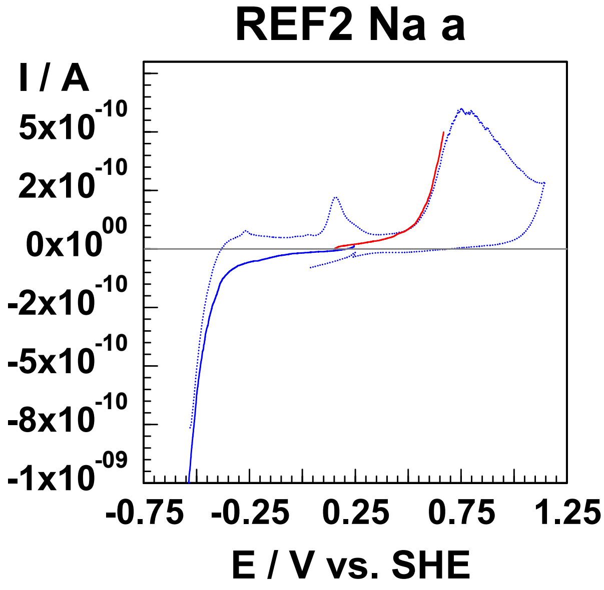


Figure 11: Voltammetric characterization of sample **REF2 Na a** at a a PtUME (50 µm)

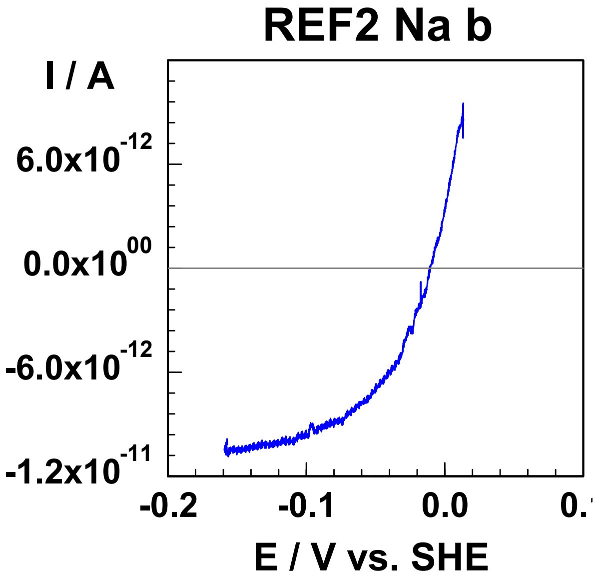


Figure 12: Voltammetric characterization of sample **REF2 Na b** at a a PtUME (50 µm)

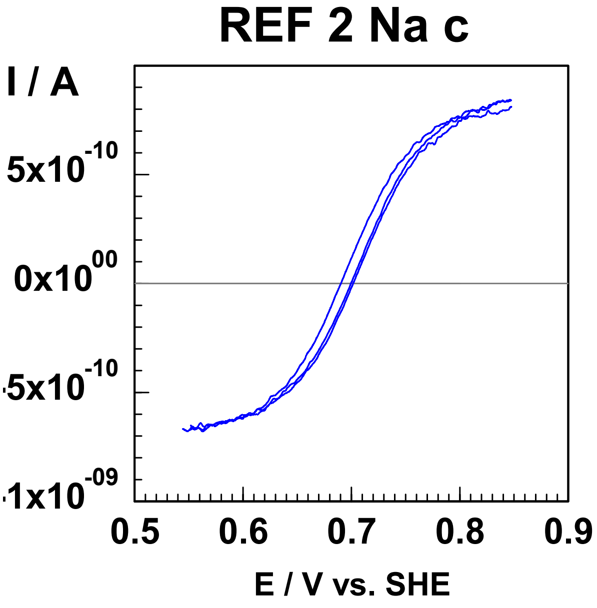


Figure 13: Voltammetric characterization of sample **REF2 Na c** at a a PtUME (10 µm)

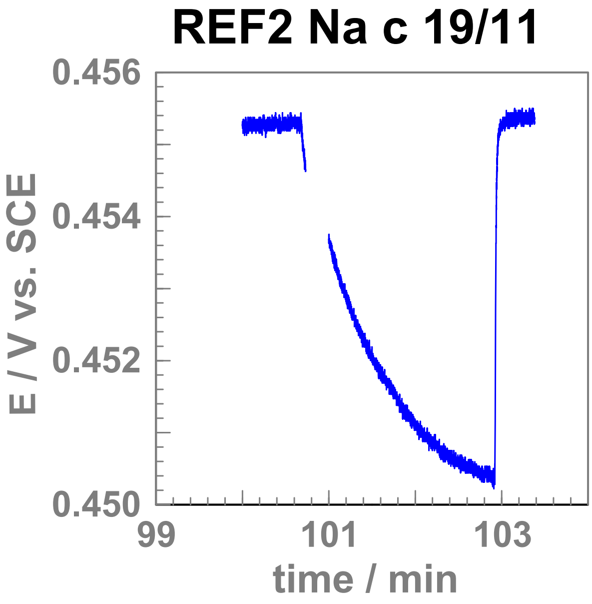


Figure 14: Potentiometric measurements performed with sample **REF 2 Na c** at a PtRDE.. Effect of the rotation rate

- The measurements made in November ’09 with sample **REF 2 Na a** must be discarded: there is a gap of about 500 mV between the potentiometric and the amperometric value. Probably, the PtUME (E = 48 mV vs. SHE) was contaminated with the mackinawite suspension that has been measured just before. As regards the potentiometric measurement (E = 514 mV vs. SHE), we do not have any credible interpretation.

The measurements performed in December ’09 with sample **REF 2 Na a** led to quite better results. The two techniques gave quasi identical potential values (amperometric at PtUME 230 mV vs. SHE and potentiometric at PtRDE 210 mV).

● During the first run of measurements, the results obtained for sample **REF 2 Na b**, that consists in an alkaline suspension of Fe(III) and Fe(II) in concentrated NaCl, are quite strange: whereas the potentiometric measurements indicate that the redox potential decreases during the transition from sample **REF 2 Na a** to sample **REF 2 Na b** (as it is expected because of the pH increase), the amperometric ones show the opposite effect. Indeed the potential passes from 48 to 111 mV vs. SHE.

This phenomenon has not been observed during the second run of measurements where both potential values (potentiometric: ~170 mV and amperometric ~-116 mV vs. SHE) are lower than these measured for sample **REF 2 Na a**. However, with sample **REF 2 Na b** the amperometric determination of potential is much lower than the potentiometric one (more than 200 mV).

● With samples **REF 2 Na a** and **REF 2 Na b** measurements have been also made at a platinum rod. The shape of the corresponding curves is quite difficult to interpret. Probably the fact that these electrodes were simply rinsed with deionised water before use is behind this fact.

Sample REF 3 HC a

(|hydroquinone|=10^{-3} M, 0.1 M NaCl, pH 5-6 (MES buffer))

As QH_2 cannot react with any component of this solution, only one constituent of the redox couple Q/QH_2 is present. Therefore, we expect that the potential measured will be not stable and without any thermodynamic meaning.

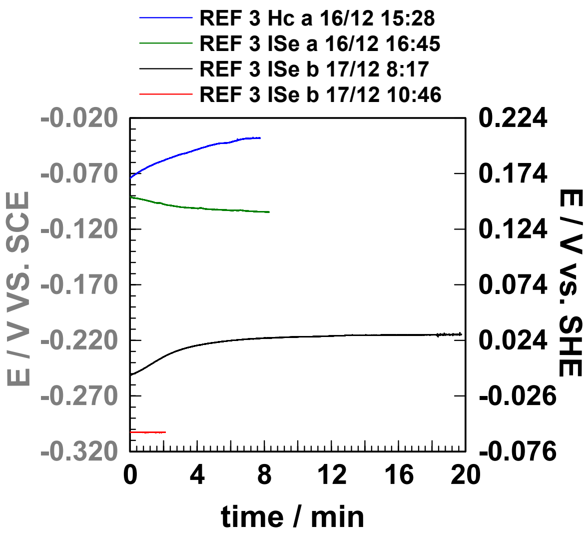


Figure 15: Potentiometric measurements performed with samples **REF 3 Hc a, REF 3 ISe a** and **REF 3 ISe b** at a.

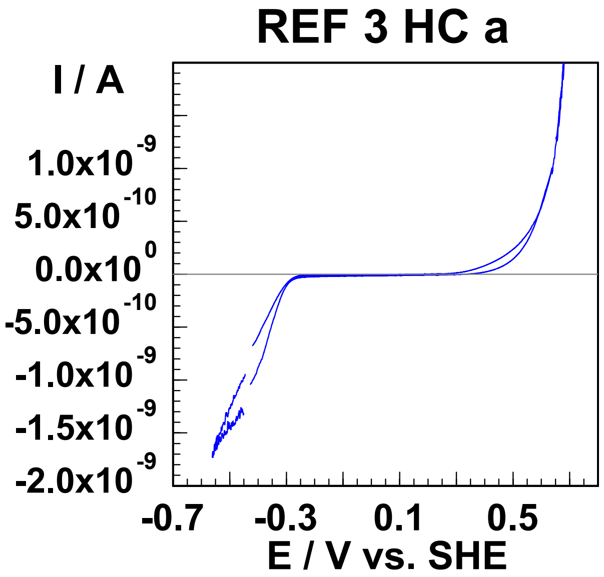


Figure 16: Voltammetric characterization of sample **REF2 Na a** at a a PtUME (50 µm)

The oxidation of $1.4BQH_2$ in the presence of MES and the reduction of H^+, free or associated with MES, are the possible electrochemical reactions at the platinum electrodes. In any case, the potential measured will be quite lower than 373 mV vs. SHE, which is the apparent normal potential for the couple $1.4BQ/1.4BQH_2$ at pH 5.5. Indeed the potential measured potentiometrically is about 200 mV vs. SHE and that measured amperometrically about 250 mV.

Samples REF 3 ISe a and REF 3 ISe b

With these samples more or less complex reactions occur when the mixtures are prepared and, before any discussion about the potentials that will be measured, we must consider these reactions.

- Sample **REF 3 ISe a**,

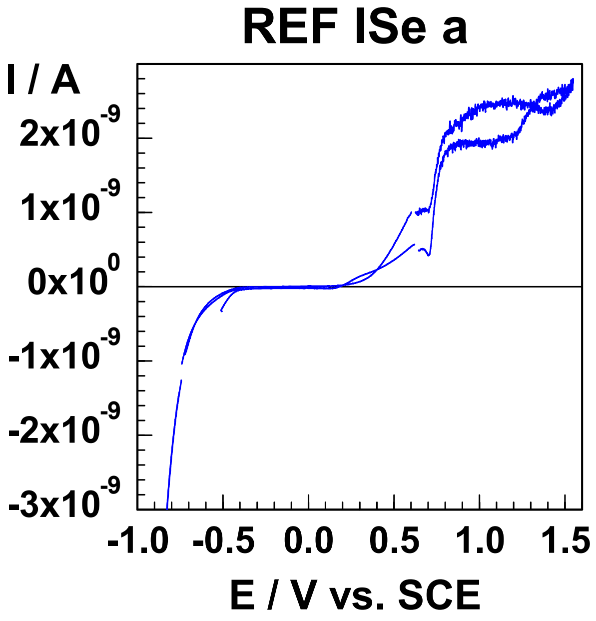


Figure 17: Voltammetric characterization of sample **REF3 ISe a** at a a PtUME (10 µm)

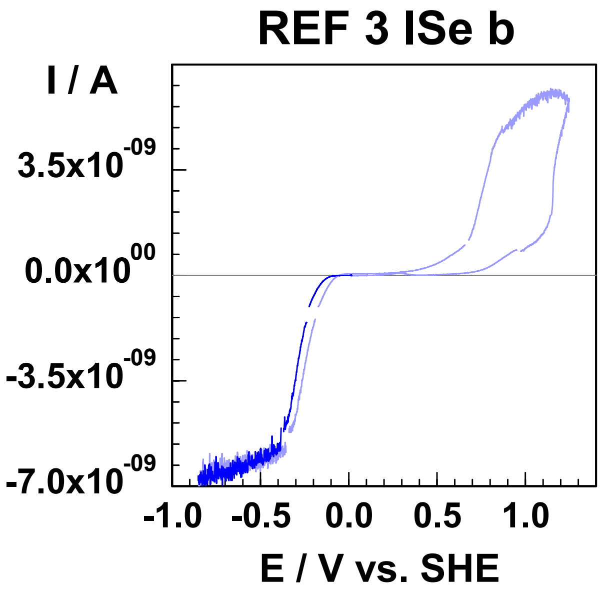


Figure 18: Voltammetric characterization of sample **REF3 ISe B** at a a PtUME (10 µm)

(|hydroquinone|=10^{-3} M + 10^{-4} M NaI and $NaIO_3$, 0.1 M NaCl, pH 8-9 (TRIS buffer))

During the preparation of the mixture, a part of $1.4BQH_2$ (apparent normal potential for the couple $1.4BQ/1.4BQH_2$ at pH 8.5 = 0.193 V vs. SHE) will react quantitatively with IO_3^- giving 1.4BQ. After reaction |1.4BQ| = 3×10^{-4} and $|1.4BQH_2|$ = 7×10^{-4}. Therefore, the theoretical potential of the solution is given by the $1.4BQ/1.4BQH_2$ system and E = 0.193 + 0.03 log 3/7 = 0.182 V vs. SHE.

- Sample **REF 3 ISe b**

(|anthraquinone|=1.6×10^{-3} M reduced by Na-dithionite) + 10^{-4} NaI, 0.1 M NaCl, pH 5-6 (MES buffer). $|AQ|/|AQH_2|$=3:1)

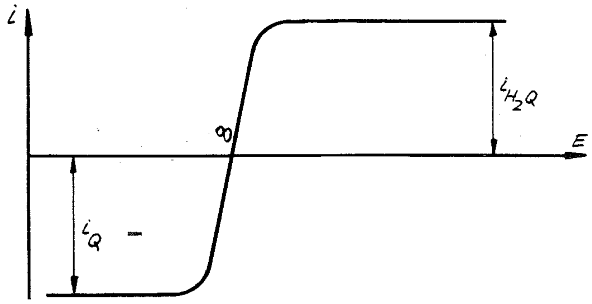


Figure 19: Theoretical voltammetric curves for the $1.4BQ/1.4BQH_2$ system in pH buffered media

Therefore, according to the data furnished, if the electrochemical system AQ/AQH_2 (apparent normal potential at pH 5.5 = -0.176 V vs. SHE) is sufficiently rapid

E = -0.176 + 0.03 log 3/1 = -0.162 vs. SHE.

In both cases, as the solutions contain in principle the two components of a rapid electrochemical system ($1.4BQ/1.4BQH_2$ or AQ/AQH_2) in pH buffered media, it is expected that: (i) the voltammetric curves will have the same shape as in fig 1A, (ii) the potentiometric and amperometric measurements will be in excellent agreement (as with samples **REF 1 (II/III) c** and **REF 2 Na c**). Therefore, the potential experimentally measured will be given by the Nernst law. However, the shape of the experimental voltammetric curves is quite different: anodic and cathodic parts are separated by about 800 mV for both samples **REF 3 ISe a** and **REF 3 ISe b** (fig 1B).

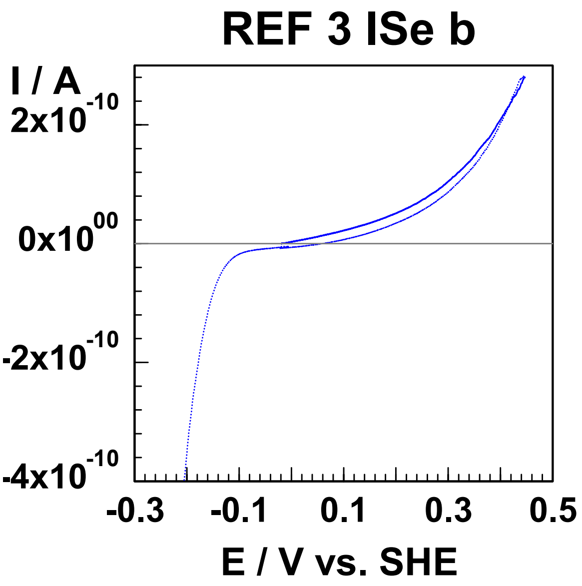


Figure 20: Voltammetric characterization of sample **REF3 ISe B** at a a PtUME (10 µm) - Detail

With **REF 3 ISe a**, the potentials determi-ned experimentally (~140 mV vs. SHE potentiometrically and ~120 mV ampero-metrically) are lower than this calculated using the Nernst law (182 mV vs. SHE). With **REF 3 ISe b**, the potentials determined experimentally (~-59 mV vs. SHE potentiometrically, whereas the potential values determined amperometri-cally fall down with time from ~31 to -53 mV vs. SHE in 100 min) are quite higher than this calculated using the Nernst law (In both cases, even when the potentials measured are close to the calculated ones (**REF 3 ISe a**), they are badly defined because they are located at the flat part of the i-E curves. This fact is probably observed because of the slow kinetics of the systems considered or of adsorption phenomena onto the electrodes.

Sample NAT 2:

Crushed COx material equilibrated with artificial COx pore water

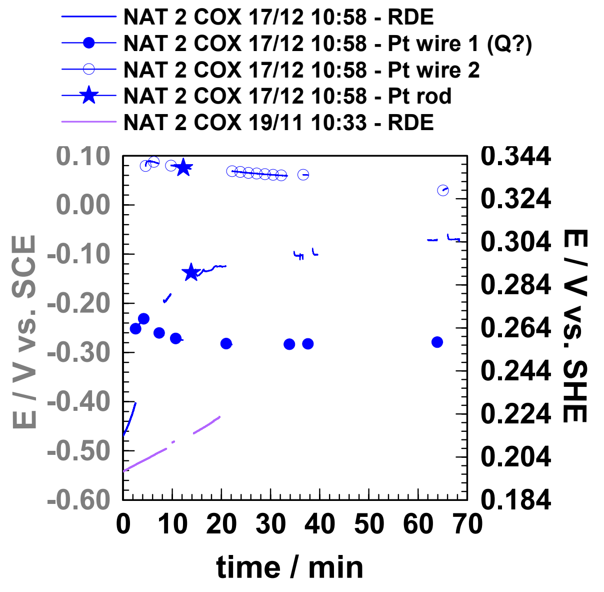


Figure 21: Potentiometric measurements performed with sample **NAT 2** at a PtRDE, Pt wire and a Pt rod.

- In November '09 the suspension of COx showed a very strange behaviour. The potential recorded potentiometrically started from a very low value (-298 mV vs. SHE) and then linearly increased with time and reached the value of -186 mV after 20 minutes. We never observed such behaviour with COx suspensions in our laboratory (usually the potentiometric measurements around about 200 mV vs. SHE). The amperometric measurements, that give potential values of about 100 mV more negative, confirmed this high oxidizability of the examined COx suspension. These measurements have been repeated after the replacement of the COx suspension by a fresh one, and the results were the same.

- Measurements performed in December '09 led to more realistic values: 173 mV vs. SHE potentiometrically and 130 amperometrically. Moreover, during this series of measurements three other platinum electrodes have been used. For the same reasons as previously these results will not be commented here .

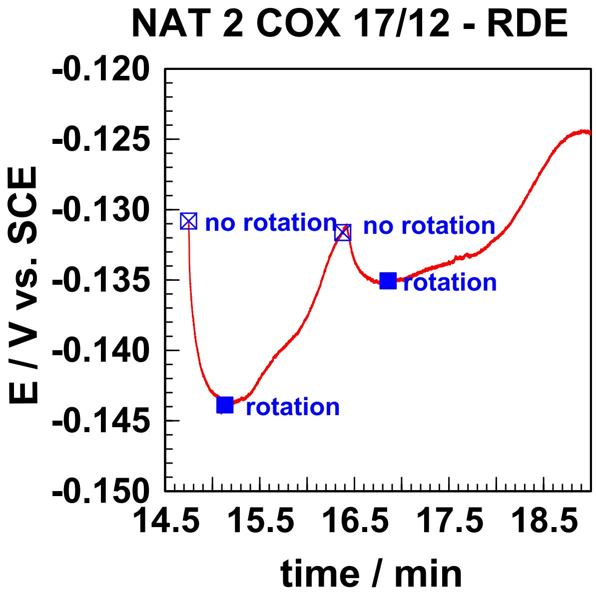


Figure 22: Potentiometric measurements performed with sample **NAT 2** at a PtRDE. Influence of the rotation rate.

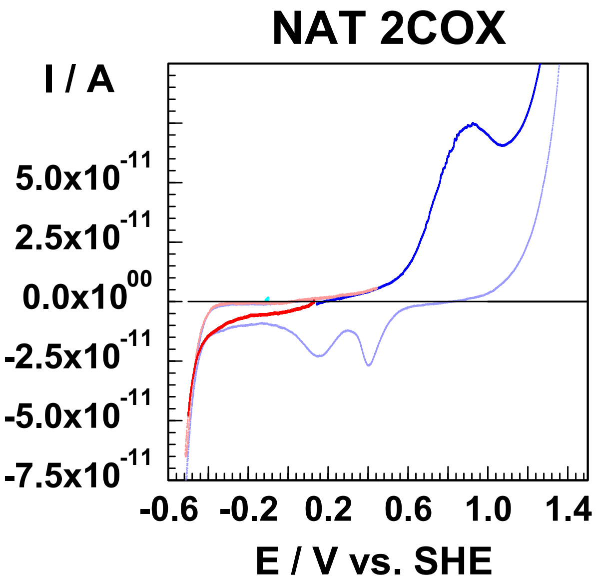
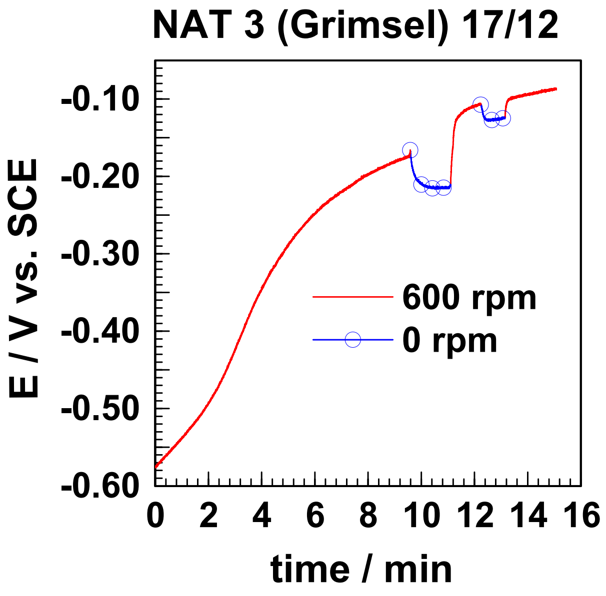


Figure 23: Voltammetric characterization of sample **NAT 2** at a a PtUME (10 µm)

The insertion of iron particles in the platinum electrodes is the most probable reason for the very low potentials measured in December '09.



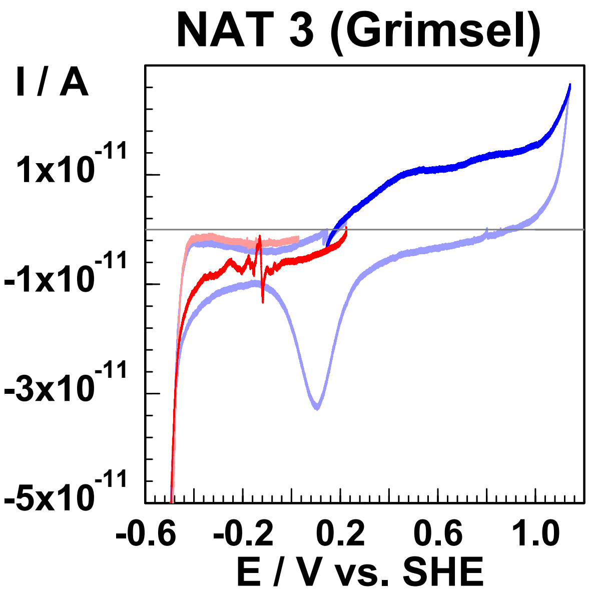


Figure 22: Potentiometric measurements performed with sample **NAT 2** at a PtRDE. Influence of the rotation rate.

Figure 23: Voltammetric characterization of sample **NAT 2** at a a PtUME (10 µm)

Sample NAT 3:

Crushed Grimsel material equilibrated with artificial Grimsel water

We observed a dramatic drift (500 mV in 15 min) at the beginning of the measurements performed potentiometrically. However, the potentiometric (157 mV vs. SHE) and the amperometric (180 mV vs. SHE) determinations led to relatively close potential values. Before any interpretation, of the potential measured the knowledge of the exact composition of the Grimsel materials is needed.

CONCLUSION

Despite some technical problems that had been encountered, we confirmed in a very different experimental environment the tendencies observed in our laboratory. Moreover, UMEs prepared by moulding platinum microwires in epoxy or polyester resins worked entirely satisfactory in concentrated brines.

As it was expected, the potentials measured using the potentiometric or the amperometric techniques are in good agreement for "redox buffered" solutions as long as complex additional phenomena do not intervene. When the samples contain very low concentrations of electroactive species, only one component of a redox system or the electrochemical kinetics is extremely slow, the potential values measured amprerometrically and potentiometrically are quite different.

In the following section we will compare our results with those obtained by the other participants. Then, we will attempt to interpret the differences observed as well as the discrepancies between potentiometric and amperometric determinations on the basis of current-potential curves which we recorded at platinum ultramicroelectrodes during this exercise. Moreover we will consider the possible influence of the experimental devices and protocols used by each participant on the data collected (See Appendixes).

One of the major objectives of a future collaboration must be the establishment of a protocol (or a normalized procedure or a standard method, whatever the term used is) for the measurement of redox potentials that will be followed by a multi-laboratory experimental validation. The purpose of this protocol will be not to measure the "exact" value of the redox potential. The purpose is that all the measurements made by different operators are inside a confidence interval that must be defined.

A posteriori, the single criticism we can make about the ICE is that the participants had almost complete freedom of action..

The only restrictions that encumber visitors were: i) the fact that a little "bulky" device could not be introduced into the glove boxes and ii) the lack of plugs other than banana and BNC. For that reasons few measurements have been made outside the glove boxes or using extra-long cables maladjusted for sensitive measurements.

For several samples, we think that, the absence of any restraint is responsible for some large differences observed in the potentiometric measurements performed by the different participants. There are many many factors that can intervene (electrodes, treatment of the electrodes, convection, "potentiometer", electromagnetic noise....) and in this way it is virtually impossible to attribute without a high degree of speculation one problem to this factor and another problem to that.

In our opinion, the simpler, cheaper and more efficient restraint is to furnish to the different partners the electrodes that must be used as well as the vessel and the stirring material for the measurements.

In this way, it can be ordered for each partner three couples of electrodes chosen in common on top of their own electrodes. Each type of electrode must by exactly the same for each partner: same company, same model and same lot of fabrication (often in electrochemical studies the electrochemical kinetics is a function of the lot of platinum used).

This constancy would make possible the appreciation of other parameters as the equipment or the way of doing own to each participant.

Some considerations on the kinetics of the electrochemical systems

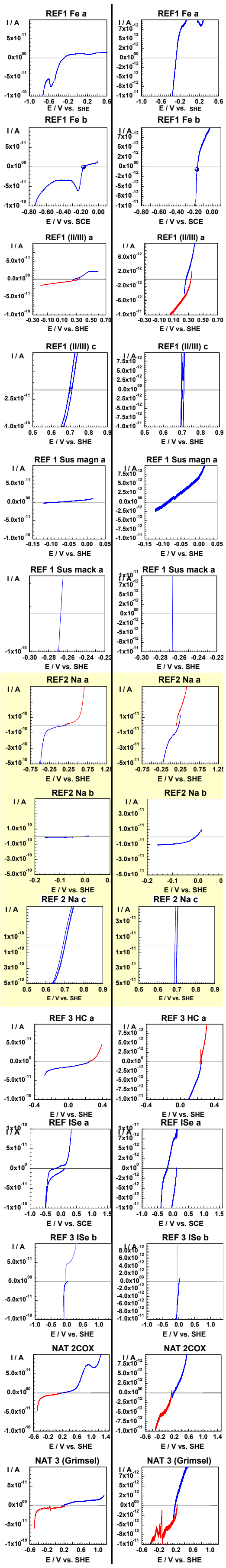


Figure X: overview of the voltammetric curves recorded. Plotted in the range of ± 100 pA and ± 10 pA (curves recorded with 10 µm Pt UME) or in the range of ± 500 pA and ± 50 pA (curves recorded with 50 µm Pt UME).

Considering the voltammetric curves which we plotted one can remark that only system that has a rapid electrochemical behaviour is the Fe(III)/Fe(II) system in acidic media (samples **REF 1 (II/III) c** and **REF 2 Na c**). Surprisingly, the samples containing a quinone/hydroquinone mixture in pH buffered media have not this behaviour.

Figure X shows an overview of the voltammograms recorded during this exercise at platinum UMEs (10 µm PtUMEs for all the measurements made, except for those recorded in brines – yellow background – where 50 µm PtUMEs has been used). By considering this figure, we immediately see that sample **REF 1 Sus. mack. A**, which contains the mackinawite suspension at pH 6, shows by far the higher exchange current after samples **REF 1 (II/III) c** and **REF 2 Na c**. This high exchange current and the fact that the mineral particles completely cover the electrode surface are responsible for the good accuracy of the measured potentials with **REF 1 Sus. mack** when the solid phase is present). Moreover, we can notice an excellent agreement between the potentiometric and the amperometric determination.

If we continue to examine the different samples in decreasing order of exchange current, one can remark that in the voltammograms for samples **REF 1 Fe a** and **REF 1 Fe b**, which consist of suspensions of metallic iron at pH 9 and 5-6, the curve intersects the horizontal axis almost vertically. For that reason, for the both samples, there is good accordance between the potentials determined by potentiometry and amperometry when the measurements are performed in close time proximity to each other. If we consider the differences observed in the potential values determined for the complete suspensions: i) by different participants, ii) by the same participant with different samplings, iii) with the same sampling at different times, these differences can be attributed, at least for a great part, to changes in the solid/liquid ratios of the suspensions.
Indeed, in addition to the parameters in relation with the reaction of the iron suspension with water that we brought up in the preceding paragraphs the following considerations can be done:
i) When the suspension particles do not completely adhere to the electrode the latter works as two short-circuited electrodes: one of platinum and the other of "iron" therefore the potential measured is a "mixed potential" without any thermodynamic meaning
ii) This mixed potential is a function of the surface area of the platinum covered by the particles and depend on:

- the amount suspended solids sampled with the liquid phase
- the convection
- settling phenomena occurring with time.

The behaviours of samples **REF 1 (II/III) a** (|$FeCl_2$| = |$FeCl_3$| = 10^{-4} M, 0.1 M NaCl, pH 5-6) and **REF 2 Na a** (|$FeCl_2$| = |$FeCl_3$| =

10^{-4} M, 5 M NaCl, pH 6-7), are quite similar. Potentiometric and amperometric measurements lead to near results if they are performed in close time proximity to each other. Since a precipitation of Fe(III) is observed shortly after the contact of the sample with the electrodes the potential recorded slowly drifts with time to lower values.

In the cases of samples **REF 3 HC a**, **REF 3 ISe a** and **REF 3 ISe b**, that contain quinones, relatively high exchange current equally appear. However, the electrodes seem to be very easily polarized during the voltammetric scans recorded with the two first samples. With sample **REF 3 ISe b**, voltammograms are quite satisfactory but our own feeling is that the composition of the solution is changing over time. Perhaps catalysis phenomena occurred at the surface of "large" electrodes that are in the solution (PtRDE and the counter electrode). The only thing that is sure is that the potential recorded at the PtUME slowly drifts towards the potential measured with the PtRDE. Further experiments are required to clarify the electrochemical behaviour of these samples.

The voltammetric curves for the natural ground compounds **NAT 2** (crushed COx material) and **NAT 3** (crushed Grimsel material) are more than satisfactory. This ends up by a relatively good accordance between potentiometric and amperometric measurements. However, if we compare the whole of the potentiometric measurements, they present a high discrepancy. There is no surprising about that considering that we previously discussed about suspensions.

The exchange current for sample **REF 2 Na b** ($|FeCl_2| = |FeCl_3| = 10^{-4}$, 5 M NaCl, pH 12) is excessively low and probably the electrodes are strongly polarized. This is behind the high discrepancy that we can notice for the whole of the measurements.

Must we stir the solution/suspension during the potentiometric measurements or not?

In our opinion the fact of stirring the samples has the advantages that follow:

- If concentrations and/or the "pulp density" change in the vicinity of the electrode, whatever the reason for this change (settling, polarization, catalysis phenomena at the electrode…) the convection tends to homogenize the sample, and the measurement is more representative.
- If the electrodes are polarized by the instrument used to perform the measurement, the convection increases the limiting current (see Appendix A) and brings closer the potential measured and the zero current potential. Moreover, if the concentration of the system that imposes the redox potential is extremely low, this increase of limiting current may prevent that the measuring instruments detect other species located at higher or lower potentials (according to the direction of the polarizing current).

APPENDIX A

Why the potential varies with the convection?
Can we correlate this variation in potential with the current that flows trough the measuring instrument?

During the analysis of the results obtained potentiometrically with sample **REF 2 Na c** ($|FeCl_2| = |FeCl_3| = 10^{-4}$, 5 M NaCl, pH 2) using the PtRDE we showed that the potential measured diminishes by about 5 mV when the rotation speed of the PtRDE passes from 600 rpm to 0. This decrease can be easily understood if we look at the voltammetric curves plotted using the Levich law which gives the limiting current in function of the rotation rate for RDEs. Figure AppA1A shows the calculated voltammograms plotted for a rapid mono-electronic electrochemical system with $|Ox| = |Red| = 10^{-4}$ M at an electrode of 2 mm in diameter with rotation rates in the range from 0.001 to 1000 rpm. If we suppose that the very small positive current i_ε[3] flows through the measurement circuit, we can see that the potential where the voltammetric curve crosses the red horizontal line i_ε (i.e. the electrode potential) increases when the rotation rate of the electrode decreases.

Figure XB is a magnification of figure XA for the y-axis. Therefore, we can see finer details near zero current. It is tempting to use this graph in order to find the i_ε value that produces a variation of 5 mV on the potential measured when the rotation rate of the RDE passes from 600 to 0.001 rpm. This value is about 4×10^{-9} A that appears as quite large. However, it is known that it is not recommended to use Levich law for rotation rates lower than 2 rpm.

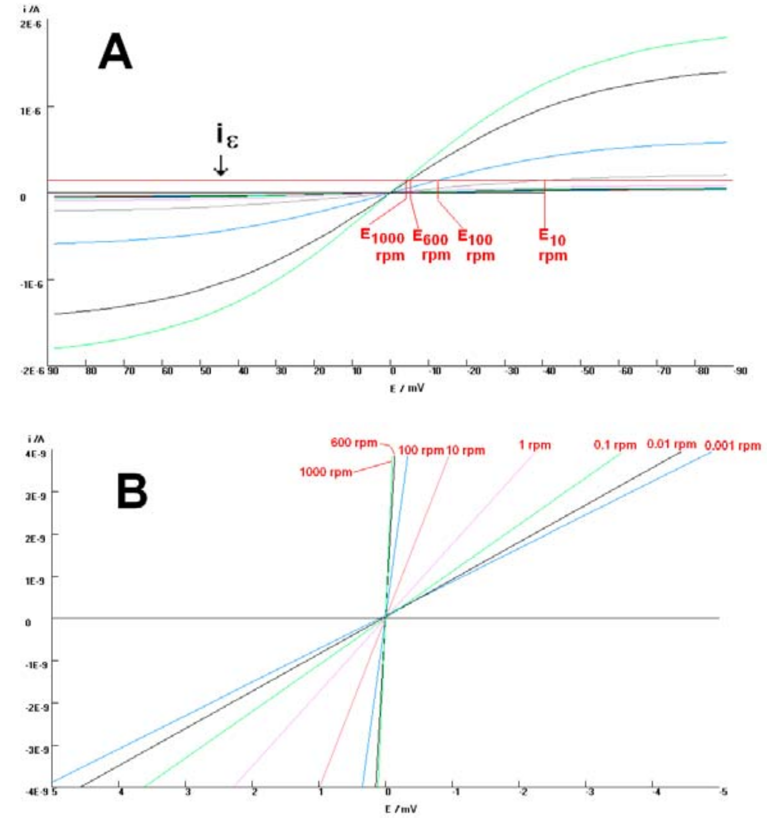


Figure AppA1: Voltammetric curves plotted according to the Levich law for a rapid monoelectronic electrochemical system with $|Ox| = |Red| = 10^{-4}$ M at an electrode of 2 mm in diameter for rotation rates from 0.001 to 1000 rpm.

There is another way to proceed in order to determine i_ε. If we assume that the electrochemical kinetics is rapid, the Nernst law is always valid, even when a current flows through the electrical circuit. Therefore, a change in the potential measured with the rotation rate of the electrode can be related to the variation of the concentrations of Ox and Red in the

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[3] The value of i_ε is greatly exaggerated here for pedagogical purposes.

vicinity of the RDE. This variation corresponds to a certain current that can be estimated with the aid of the i-E curves plotted in figure XA.
If Ox and Red are the concentrations of the species Ox and Red in the solution and Ox' and Red' the concentrations of Ox and Red close to the surface of the electrode, we can write:

$\log(Ox/Red) - \log(Ox'/Red') = \log(OxRed'/Ox'Red) = \Delta V = 0.005$ V
and $Ox = Red = 10^{-4}$ M.

If x is the amount of Ox transformed into Red: $Ox' = Ox - x$ and $Red' = Red + x$, we can write:
$Ox(Red+x)/(Ox-x)Red = 10^{\Delta V} = 1.0116 = \mathrm{A}$
$OxRed + xOx = \mathrm{A}OxRed - x\mathrm{A}Red$
$OxRed(1-\mathrm{A}) = -x(\mathrm{A}Red+Ox)$

In this way:
$x = OxRed(\mathrm{A}-1)/(\mathrm{A}Red+Ox) = OxRed(1.0116-1)/(1.0116Red+Ox)$

As $\mathrm{A}Red \approx Red$:
$x \approx OxRed(0.0116)/(Red+Ox) \approx 1\times10^{-8}(0.0116)/(2\times10^{-4}) = 5.8\times10^{-7}$ M

That means that about 0.58% ($5.8\times10^{-7}/1\times10^{-4}$) of the initial concentration of Ox have been transformed at the electrode surface with the stopping of the rotation of the RDE.

If the polarization current i_ε is responsible for the change of the concentrations on the electrode surface this effect, the amount of electroactive species concerned by this transformation will be same whatever the rotation speed of the electrode. will be the same about 15 times less important when the electrode is rotating. Therefore we can assume that

If the polarization current i_ε is responsible for the change of concentrations on the electrode surface, the amount of electroactive species concerned by this transformation will be the same whatever the rotation speed of the electrode. In this way, the percentage of electroactive matter that arrives at the electrode and is concerned by this transformation will be quite lower (about 15 times) when the electrode is rotating. Fort that reason we will assume that the electrode is concerned by the polarization phenomenon only when it does not rotate.

When the electrode is stationary, an electroactive species 1×10^{-4} M produces a limiting current of about 4×10^{-8} A. Therefore, the concentration of 5.8×10^{-7} M correspond to a current $i = 0.0058 \times 4\times10^{-8} = 2.32\times10^{-10}$ A.

In this way, the value of 2.32×10^{-10} A for i_ε is more reasonable.

APPENDIX B

In order to check if the nature of the apparatus used for the potentiometric determinations could have an influence on the measurements performed, we tested a dozen of commercial instruments by measuring the current that flows through the instruments when they operate.

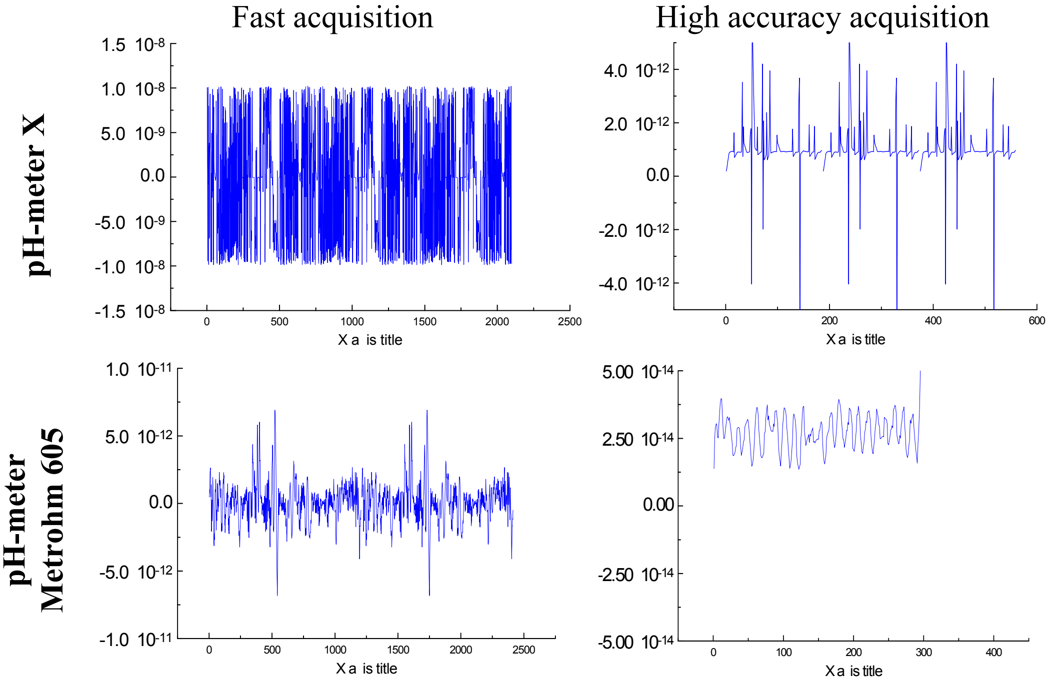

Figure AppB1: Comparison of the performances of two commercial millivoltmeters

We represented in figure AppB1 the results for the best and the worst of the apparatus tested. Two types of measurements have been carried out. The first is a very fast measurement (one point every ms) that allows to have an idea about the whole of the currents that flow through the measuring instrument. The second one is a measurement of high accuracy that allows to obtain the mean value of these currents.

We can remark two things: i) during the fast measurements oscillations of high frequency are detected. The magnitude of these oscillations may be of 10 nA for the worst apparatus, and they are limited to less than 5 pA with the best one (factor of 1000), ii) the mean current values, which are usually provided with the characteristics of the instruments, vary from about 25 fA to 2 pA. Moreover, this current can be positive or negative according to the instrument used. The “best” instrument is an analog millivoltmeter of about 20 years old and the worst a digital one, with high pretensions and quite expensive.

The relatively high currents that flow when certain devices are used, which can polarize the electrodes, must be taken into account during the interpretation of potentiometric measurements.

ReCosy, Intercomparison Exercise

Within Workpackage 2 “Development of redox determination methods”

Short summary description

CTH (5): Agreement between measured Eh and quantification of oxidation states

S. Allard, C. Ekberg, S. Holgersson, G. Skarnemark, K. Spahiu and A. degaard-Jensen

Background and Objectives

The equilibrium indicated in the measurement of Eh is presumed to occur at the electrode surface. A true redox potential occurs when the chemical potential due to differences in concentration of reduced and oxidized species is equal to the potential difference between the reference and platinum electrodes and there is no net flow of electrons. It is of importance to realize that the investigated deep geological waste disposal sites systems may not be at perfect, or near perfect equilibrium. Chemical reactions occur at different rates and the equipment used to register Eh and pH has built in errors and biases. In a more complex system with several redox participants, a perceived equilibrium with a net zero current, may in fact be a summation of potentials that results in a pseudo-equilibrium.

The present study aims at measuring the Eh in the received ICE samples with electrodes in the same way that will be used for our other samples within the ReCosy project.

Our results can thereafter be evaluated and compared to the results of the other project partners and possible systematic errors identified. This is also important because the planned investigations by Chalmers within the main part of the ReCosy project will include actual quantification of the various oxidation states of certain elements (Fe, U, Pu, for example) in artificial groundwater systems. A relation of the oxidation states to the Ehs as indicated by electrode measurements, will be established.

Experimental method and approach for measurements with redox electrode

Measurements with a commercial combination electrode with Pt working electrode and Ag/AgCl reference electrode (Mettler-Toledo InLab Redox Micro) was made. Before the measurement, the electrode condition was checked with a redox buffer solution (Mettler Toledo 220mV for Ag/AgCl ref at 25°C). The response slope of the electrode was checked with pH buffers saturated with quinhydrone. The actual measurement of a sample was made for a maximum of 15 minutes. New measurements of each sample was made over the next couple of days in order to have a mean value with at least three measurements.

All measurements was made in a N_2 filled glove box (MBraun UniLab, O_2~ 1ppm).

Solutions measured

The samples provided to us were:

REF 1 Fe b: 0.1M NaCl with 100mg Fe powder and MES buffered to pH 5-6.

REF 1 (II/II) a: 0.1M NaCl with 1:1 $FeCl_2$:$FeCl_3$ (0.1mM) and MES buffered to pH 5-6.

REF 3 HC a: 0.1M NaCl with 1mM hydroquinone and MES buffered to pH 5-6.

REF 3 ISe a: 0.1M NaCl with 1mM hydroquinone and TRIS/0.1mM NaI/0.1mM $NaIO_3$ buffered to pH8-9

REF 4 ACW1: hyperalkaline, 0.1 mM Ca, 10mM Si, 110mM Na, 180mM K.

REF 4 ACW2: hyperalkaline, 10mM Ca, 0.01mM Si, 110mM Na, 180mM K.

NAT 1a: Gorleben groundwater, diluted. Includes humic acids.

NAT 2: Crushed Clay-Rock material equilibrated with artificial porewater

NAT 3: Crushed Grimsel material equilibrated with artificial porewater

Expected outcome

The measurements performed are expected to be in relative agreement to values obtained by the other project members.

Outcome of the study

The ICE samples were sent to CTH and measured in our laboratory about one month after the actual ICE excercise in Karlsruhe. For a detailed account of the results of the CTH measurements see the separate report. Apart from the general conclusions and recommendations regarding the ICE excersise, given in the main text, some additional comments can be made about our results.

The electrode measurements were generally found to work well. However, the contamination problem, with associated memory effects, was more severe than expected. This was especially the case when measuring the hyperalkaline REF4 waters.

No attempts were made to replace the electrolyte, instead it was cleaned by leaving the electrode immersed in a bulk solution of fresh electrolyte overnight.

This memory effect reinforces our conviction that redox measurements with this type of electrodes should not be made where the electrode is immersed in sample for extended periods of times. If non-equilibrium is suspected, renewed short-time measurements should be made over the next few days.

The repeated measurements gave fairly constant values. Standard deviations were 10-20mV for the redox-buffered reference samples, while they were 10-70mV for the natural waters. As expected, the natural waters were more troublesome to get a stable reading for.

However, this does not change our view that only short-time measurements with conventional redox electrodes should be made. If continous redox monitoring is to be made, another electrode system (that is: another reference electrode system) should be used that is not prone to degradation over time.

In the context of what seems to be a general problem in the ICE outcome of a drifting response it is important to try to identify the source of this behaviour. Is it:

1) a system problem. This is the case of non-buffered system with typical redox couples O_2/H_2O, NO_3/N_2, NO_3/NH_4^+, SO_4/HS^-, CO_2/CH_4 which all exhibit kinetically slow reactions. This means they will not give any measureable current and/or will probably not be in equilibrium. Attempts to measure redox equilibrium in such a system with ordinary redox electrode are therefore bound to fail.
2) an electrode problem. It is a well known fact that Pt is prone to form oxides which in turn will delay the reading. However, it will not change the final reading, once it is established. This problem can be suspected if a drift is measured also in redox-buffered systems, but only then. The cure is usually to clean the Pt surface with HCl and by polishing. Take note of the potential contamination of electrolyte with HCl.
3) a sample problem. When samples are prepared they immediately start to equilibrate with the local atmosphere. This may take a while and it is therefore recommended to either measure as soon as possible if this equilibration with the atmosphere is not desired. On the other hand, if equilibration is desirable the measurement session should be extended over several days with several short-time measurements. This is also an issue when measuring foreign samples, prepared at other laboratories or samples taken in natural surroundings. In such case the original atmosphere skould be preserved. This can be accomplished by using septum wich allows a gas-tight immersion of the glass electrode.

Only by the recognition of which source may be the cause of the drifting response, the correct action can be taken.

InterCompEx

Report and evaluation of the redox potential measurements during the Intercomparison Exercise of ReCosy

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Background and Objectives

Within ReCosy the chemical and redox behavior of radionuclides, e.g. uranium, in different systems through microbial mediated processes are investigated by FZD. For this purpose measurements of oxygen concentration and redox potential of biological systems are necessary. In-situ studies on the redox potential of biofilms grown in acid flooding water of the former uranium underground mine in Saxony (Germany) were conducted for the first time by electrochemical microsensors. The results indicate oxidizing conditions within the biofilms, but nevertheless the accuracy of the measured redox potential is not confirmed since comparable studies do not exist.

The aim of the present study is the reproducibility testing of the redox potential values obtained by the used redox microsensor with emphasis of systems with microbiological activity and organic compound.

Experimental method and approach

For redox potential measurements a miniaturized platinum electrode from Unisense (Denmark) with a tip diameter of 10 µm was used. The electrode was connected via a high-impedance millivolt-meter to a reference electrode, which was immersed in the same solution as the electrode. The reference electrode was a simple open-ended Ag/AgCl electrode with a gelstabilized electrolyte, saturated with 1 M KCL. In general, the reference electrode is used to establish a reference potential against the redox microelectrode. The redox microelectrode was checked for its function by different quinhydrone redox buffer solutions (pH 4 and 7) by exposing both, redox electrode and reference electrode, in the same buffer before and after the measurements of one set of samples. As the redox microelectrode is sensitive to temperature, the calibration and the measurements were performed at the same temperature by inserting both electrodes into the same sample/solution. The redox electrode had been cleaned before the measurements by immersing it in nitric acid (1:1 H_2O) for about 30 minutes. The reference electrode was submerged in 70% ethanol for a couple of minutes and rinsed afterwards with 1M KCL. Between the measurements, the reference electrode was stored in 3 M KCl. The redox electrode was left in pure water. The measurements were not conducted in an Ar inert gas box, but with regard to anoxic conditions, the samples were hold in a tube, which was ventilated by Ar. The redox potential of the samples was recorded after the signal was stable, but at the latest 15 minutes after the beginning of the measurement. Since the sensor signal is very dependent on temperature, the temperature of the samples was controlled permanently during the measurements. The obtained values of the redox potential were corrected after Camman and Galster (1997), dependent on the temperature and the molar concentration of the electrolyte of the reference electrode and listed in the following tables.

In order to control the drifting of the signal a controlling system was established. First, a grounding system was guaranteed. Next, the high-impedance millivolt-meter was connected by an A/D converter for data acquisition with the program PROFIX (Unisense, Denmark) for controlling purpose. Before the redox electrode was brought into the different solutions the maximum and minimum values of the amplitudes were checked over a period of time controlling the stability. Subsequently, the measurements were performed in the solutions.

Solutions measured

(1) Systems with simple organics:
  - REF 3 HC a, Hydroquinone, 10^{-3} M Hydroquinone, pH 5-6 fixed with MES buffer
  - REF 3 ISe a, Hydroquinone, 10^{-3} M Hydroquinone, pH 8-9 fixed with TRIS, + 10^{-4} M NaI and $NaIO_3$
  - REF 3 ISe b, Anthrahydroquinone, Anqui:Anthyqui = 3:1 (total $1{,}6 \times 10^{-3}$ M) reduced by Na-dith., pH 5-6 fixed with MES, + 10^{-4} M NaI

(2) Groundwater with humic substances:
  - NAT 1a, Gorleben Soft Humic Rich Groundwater, S102-2227 (RCM 80), conditioned in a fridge since 03.07.1991
  - NAT 1b, Gorleben, Deep Channel Brine, S218-944 (RCM 91), conditioned in a fridge since 02.12.1993

(3) Clay-rock systems:
  - NAT 2, sample with COX characteristics

(4) Granitic groundwater (Grimsel):
  - NAT 3, sample with Grimsel characteristics

(5) High salinity / brine conditions:

- NAT 4, magnesium rich high salinity brine

(6) Homogenous systems with microbiological activity:

- MIC A1, sulphate reducing bacteria medium with growing *Desulfovibrio aespoeensis*
- MIC A2, sulphate reducing bacteria medium, sterile
- MIC B1, autotrophic acetogenic medium with growing *Acetobacterium carbonolicum*
- MIC B2, autotrophic acetogenic medium, sterile

Results

The aim of the intercomparison exercise was the testing of the accuracy and reproducibility of the redox potential obtained by a standard Pt electrode, which is used for studies on the redox behavior of radionuclides in microbial mediated processes, e.g. biofilms. The samples were chosen with respect to this subject with emphasis on systems with microbiological activity and organics. During the measurements a drifting of the redox potential was noticed in almost every sample over a short period of time. In the majority of the cases the values were stable with a tolerance after 15 minutes. In samples with high salinity the redox potential shows a drift over an extended period of time (NAT 1b, NAT 4). In microbial samples the signal needs a longer time for getting stabilized.

Tab. 1: (1) Systems with simple organics

No.	Sample description	Eh [mV]	remarks	Temp. [°C]
REF 3 HC a	Hydroquinone, pH 5-6	**285**	after 15 min.	19,8
REF 3 Ise a	Hydroquinone, pH 8-9	**165**	after 15 min.	18,7
REF 3 Ise b	Anthrahydroqu.	**10**	after 30 min.still decreasing	19,1

Tab. 2: (2) Groundwater with humic substances

No.	Sample description	Eh [mV]	remarks	Temp. [°C]
NAT 1a	Gorleben groundwater, dilute, very much humics	**193**	after 15 min.	16,8
NAT 1b	Gorleben groundwater, saline	**336**	after 30 min. still decreasing	19,2

Tab. 3: (3) Clay-rock systems

No.	Sample description	Eh [mV]	remarks	Temp. [°C]
NAT 2	Clay rock system, COX	**279**	after 15 min.	19,8

Tab. 4: (4) Granitic groundwater (Grimsel)

No.	Sample description	Eh [mV]	remarks	Temp. [°C]
NAT 3	Granitic groundwater, Grimsel	**195**	after 15 min.	19,8

Tab. 5: (5) High salinity / brine conditions

No.	Sample description	Eh [mV]	remarks	Temp. [°C]
NAT 4	High salinity - brine conditions	**674**	after 30 min. still increasing	20,2

Tab. 6: (6) Homogenous systems with microbiological activity

No.	Sample description	Eh [in mV]	remarks	Temp. [°C]
MIC A1	Desulfovibrio aespoeensis -SRB-medium	**-135**	after 30 min.	17,8
MIC A2	SRB-medium	**-84**	after 15 min.	18,1
MIC B1	Acetobacterium carbin. - AA-medium	**-119**	after 30 min.	17,6
MIC B2	AA-medium	**-108**	after 15 min.	18,2

Results compared with other groups

The redox potential values, which were measured by FZD, were compared to the results of other groups concerning their accuracy and reproducibility. In the focus of the consideration the groups were chosen in respect to similar results to the results obtained by FZD. The near-natural, and natural ground- and porewater samples (NAT) were measured by 10 to 19 different groups or redox sensors. Similar values have been achieved from FZD, PSI, INE Walther, INE Huber, MSU INE, GRS and AMPHOS, KAIST for most of the samples as shown in the following tables.

Tab. 7: REF 5 NAT 1a (pH neutral low salinity, high DOC groundwater Gohy-2227)

	FZD	**INE Walther**	**PSI**
	single Pt	Pt comb.	suspension
t (min)	15	17	10
Eh [mV]	193	219,1	187,6
T [C]	16,8		
comments	signal stable	signal decreasing	signal stable

Tab. 8: REF 5 NAT 1b (pH neutral high salinity, low DOC groundwater Gohy-944)

	FZD	**INE Huber**			**INE Walther**	**GRS**
	single Pt	single Pt	single Au	single GC	Pt comb.	com. Pt, unfiltered
t (min)	30	15	1300	1260	31	35
Eh [mV]	336	355,3	353	368,6	332	350,92
T [C]	19,2	22,5 C	22,5 C	22,5 C		
comments	almost stable	signal increasing			signal stable	signal stable

Tab. 9: REF 5 NAT 2 (natural Callovo-Oxfordian clay rich rock mineral, crushed and conditioned with artifical porewater)

	FZD	**INE Walther**	**PSI**
	single Pt	Pt comb.	suspension
t (min)	15	17	15
Eh [mV]	279	277,4	249,2
T [C]	19,8		22,5
comments	signal stable	signal stable	signal decreasing

Tab. 10: REF 5 NAT 3 (natural Grimsel crystalline rock material, conditioned with artifical Grimsel water)

	FZD	**INE Huber**			**INE Walther**	**PSI**	**MSU INE**
	single Pt	single Pt	single Au	single GC	Pt single.	1. measurem.	Protocol 4
t (min)	15	15	15	15	63	10	10
Eh [mV]	195	234	128,6	193,6	237,2	242,2	252
T [C]	19,8					22,5	
comments	signal stable	signal increasing	signal stable	signal decreasing	signal stable	signal stable	signal stable

Tab. 11: REF 5 NAT 4 (magnesium rich, high salinity brine solution)

	FZD	**INE Walther**	**PSI**	**GRS**	**MSU INE**	**AMPHOS, KAIST**
	single Pt	Pt comb.	1. measurem.	comb. Pt	Protocol 4	1. measurement
t (min)	30	31	90	10	30	35
Eh [mV]	674	644	575	685,56	657	664
T [C]	20,2					25
comments	almost stable	signal stable	signal stable	signal stable	signal stable	signal stable

In table 7 it is clearly shown, that the measurements of FZD, INE Walther and PSI are similar within the range of 187.6 mV - 219.1 mV. The same groups are showing similar redox potential values measured in the Callovo-Oxfordian clay rich rock mineral (s. Tab. 9). The measurements are ranging from 249.2 mV to 279 mV. However, the measurements in the Grimsel crystalline rock material and in the magnesium rich and a high salinity brine solution showed larger measurement ranges between 195 mV and 242.2 mV (s. Tab. 10) and 575 mV to 674 mV (s. Tab. 11), performed by the same groups.

When adding the results of some other groups with similar values the measurement range increases. Concerning the natural Grimsel crystalline rock material INE Huber have measured with a single Au electrode 128.6 mV (s. Tab. 10) with a stable signal. MSU INE showed the highest values with 252 mV. Consequently, the measurement range is enlarged from 128.6 mV to 252 mV. Even the measurements performed in the magnesium rich solution with high salinity brine (s. Tab. 11) shows a larger range from 575 mV (PSI) to 685.56 mV (GRS).

For all of these 9 groups or redox sensors the reproducibility of the redox potential in near-natural, and natural ground- and porewater (NAT) is given as long as a measurement range as mentioned above is accepted. For the natural Grimsel crystalline rock material, conditioned with artifical Grimsel water and the magnesium rich, high salinity brine solution the best accordance of the values are given.

Only one sample of the microbial systems (MIC) has been measured by redox sensors. Unfortunately, the results of the three groups (FZD, MSU INE and PSI) are not comparable. As shown in table 12 each group described a decreasing signal after 30 and 90 minutes, respectively. Consequently, redox potential measurements of microbial systems need much more time for getting a stable signal due to microbially influenced processes.

Tab. 12: Desulfovibrio aespoeensis - SRB-medium

	FZD	**MSU INE**	**PSI**
	single Pt	Protocol 1	
t (min)	30	30	90
Eh [mV]	-135	-235	-266,4
T [C]	17,8	22,5	22,5
comments	signal decreasing	signal decreasing	signal decreasing

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Conclusion

The redox potential measurements were performed in systems with simple organics, near-natural, and natural ground- and porewater samples (NAT) and in microbial systems (MIC). As an example the results of the natural ground- and porewater samples (NAT), which were obtained by 10 to 19 groups or redox sensors, were interpreted in detail. Nine groups or redox sensors, including FZD, showed similar results. In most cases the measurements varied insignificantly. In some samples a difference of approximately 100 mV between the lowest and the highest value was determined. Accepting the measurement ranges, the results will give a good overview of the redox conditions in the near-natural, and natural ground- and porewater samples. However, in special cases further studies are needed for the interpretation of the measured redox potential, e.g. Extended X-ray Absorption Fine Structure (EXAFS), TEM in combination with Electron Energy Loss Spectroscopy (EELS) and Confocal Laser Scanning Microscopy (CLSM)/Laser Induced Fluorescence Spectroscopy (LIFS).

Unfortunately, only one of the microbial system samples was studied. The results showed clearly that redox potential measurements of microbial systems need much more time for getting a stable signal due to microbially influenced processes.

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ReCosy, Intercomparison Exercise, Within Workpackage 2 “Development of redox determination methods”

KIT-INE, FZD-LGIT: Comparing the impact of measuring in suspension, after centrifugation and after ultra-filtration on the obtained pe and pH values and comparing with pe-values calculated from photo-spectrometrically determined Fe(II) and Fe(III) concentrations

David Fellhauer, Regina Kirsch

Background and Objectives

To study the interaction of (Fe containing) minerals with actinides and in particular the impact of contact between the mineral and the actinide under investigation on the redox state of the latter, aqueous suspensions of minerals to which a relatively small amount of the actinide is added are commonly used. As the oxidation states of actinides also strongly depend on the redox milieu in solution, measurement of pH and redox potential pe ($pe = 16.9\ E_h$ at 298 K) of such suspensions is of fundamental relevance (in order to describe experimental findings in terms of thermodynamics). In a previous study we noticed that the pe values obtained by measurement with a combination Pt electrode directly in contact with the suspended particles or in the supernatant solution after centrifugation differ from each other by sometimes up to 7 pe units (≈ 400 mV).

Subject of the present study is to investigate the impact of different measurement conditions on the obtained pe values of several Fe containing suspensions. The redox potential of each sample is determined with a Pt-combination electrode under three conditions:

a) with the solid particles (if any present) suspended,
b) in the supernatant solution after sedimentation of solid particles by centrifugation,
c) in the clear solution after phase separation by 10kD ultrafiltration.

Redox potentials can also be obtained from calculations based on experimentally determined concentration ratios of redox-couples. In principal, Fe(II) and Fe(II)/Fe(total) can be determined spectro-photometrically, for example with the ferrozine-method (Viollier et al., 2000). It is however not trivial to determine Fe(II) and Fe(III) concentrations with good precision if one of the redox states is in large excess compared to the other and accounts for almost all of the dissolved iron present. In addition, in the case of solutions with high ionic strength, speciation calculations to account for complexation and hydrolysis effects on iron speciation become also more complicated and less reliable. In aliquots of the ultra-filtrated solutions, Fe(II) and Fe(tot) concentrations are determined with the ferrozine-method as input data for calculations of the redox potential.

Experimental method and approach

All measurements were carried out in an anoxic glovebox with O_2-levels of about 0-10 ppmv at 22 ± 2°C. As there was no centrifuge present inside the glove box, samples had to be taken out in tightly closed centrifuge tubes for centrifugation. The samples were analyzed for pH using a combined glass electrode with ROSS reference system (Orion) calibrated against pH standard buffer solutions (Merck). Redox potentials E(V) were measured with a Pt combination electrode with Ag/AgCl reference system (Metrohm, reference electrolyte 3 M KCl) and converted into E_h according to E_h = E(V) + 0.208V at 23°C and 3 M KCl. In between measurements, the electrodes were rinsed with deionised water, put into 0.2 M HCl for about 30 seconds, rinsed again with deionised water und dried with a wipe. Measurements in suspension and after ultra-filtration (10kd) were carried out with stirring of the suspension or solution; after centrifugation the vessel containing the sample is manually slightly moved around the electrode so as to avoid re-suspending the solid at the bottom. Aliquots of the ultra-filtrates were taken as is or diluted appropriately to be measured in a spectro-photometer after complexation with ferrozine or complexation with ferrozine and reduction of Fe(III) to Fe(II) by NH_2OH HCl to obtain total iron concentrations.

Because of the high number of samples and shortness of time, the measurement time of redox potentials is limited to approx. 40 min, after which for most samples a relatively stable value was reached (drift < 0.5 mV / min).

Solutions measured

REF_1 Fe a, Fe powder, ~100 mg/L, pH not buffered (~9)

REF_1 Fe b, Fe powder, ~100 mg/L, pH 5-6, fixed with MES buffer

REF_1 (II/III) a, Fe(II) : Fe (III) = 1:1, 10^{-4}M each (at the beginning), pH 5-6 (MES)

REF_1 (II/III) c, Fe(II):Fe (III) = 1:4, total Fe 5 10^{-4}M (at the beginning), pH 2 (HCl)

REF Sus magn a, 3.1 g/L in 0.1M NaCl, pH about 6

REF Sus magn b, 3.1 g/L in 0.1M NaCl, pH about 8

REF Sus mack a, 1.4 g/L in 0.1 M NaCl, pH about 6

REF Sus mack b, 1.4 g/L in 0.1 M NaCl, pH about 8

Expected outcome

We hope to gain some insight into how much pe values obtained under different measurement conditions may vary and how this variation relates to the nature of the sample, its pH and concentrations of dissolved iron species. We do not expect to be able to draw but very limited conclusions as to the mechanisms involved in creating those pe variations.

Outcome of the study

General: In most of the samples a constant potential was reached within 40 min (drift < 0.5 mV / min). As expected the more alkaline sample of each pair of similar samples showed a more negative redox potential.

Table 1. pH and redox potential E_h and pe (versus standard hydrogen electrode and in terms of electron activity, respectively) measured in the eight samples investigated. The indices *su*, *ce* and *ul* describe the measurement condition used (*su* = in suspension, *ce* = in the supernatant after centrifugation, *ul* = in the 10kD ultrafiltrate).

sample	**pH (su / ce / ul)** $^{1)}$	E_h **(su / ce / ul) mV** $^{1)}$	**pe (su / ce / ul)** $^{1)}$	**Δ (**$E_{h,min} - E_{h,max}$**)**
REF 1 Fe a	8.91 / - / 8.18	-349 / -231 / -74	-5.90 / -3.90 / -1.25	275 mV
REF 1 Fe b	6.93 / 6.97 / 7.00	-307 / -94 / -87	-5.19 / -1.58 / -1.48	220 mV
REF 1 Fe(II/III) a	5.24 / 5.25 / 5.30	+42 / +19 / +279	+0.71 / +0.31 / +4.71	260 mV
REF 1 Fe(II/III) c	2.47 / 2.44 / 2.48	+698 / +452 / +685	+11.80 / +7.64 / +11.57	233 mV
REF Sus magn a	5.51 / 5.60 / 5.65	+66 / +70 / +96	+1.12 / +1.18 / +1.63	30mV
REF Sus magn b	7.90 / 7.73 / 7.82	-272 / -49 / -47	-4.60 / -0.82 / -0.80	225 mV
REF Sus mack a	6.65 / 6.83 6.78	-236 / -163 / +18	-3.99 / -2.75 / +0.31	254 mV
REF Sus mack b	8.36 / 8.14 / 8.16	-301 / -202 / -51	-5.09 / -3.41 / -0.87	250 mV

1) su = suspension, ce = centrifugation, ul = 10kD ultrafiltration

For 6 of the 8 samples investigated (*REF_1Fe a*, *REF_1Fe b, REF_1 (II/III) a*, *REF Sus magn b*, *REF Sus mack a*, *REF Sus mack b*) we observed a difference of about 250 mV (4.2 pe units) between the highest and lowest obtained E_h values: in all cases, the lowest value was measured in suspension, the highest after ultrafiltration. The E_h values after centrifugation, however, do not show such a systematic trend: for these 6 samples the data determined are either intermediate, close to the ultrafiltration or close to the suspension values. One reason may be that the centrifugation step is not an unambiguous technique compared to the other two methods used (the following argumentation implies that the amount and size of particles present during the measurement and possibly in contact with the electrode influence the latter): measurement in the 10kD-ultrafiltrate goes along with a complete absence of suspended particles (including colloids), measurement in suspension is characterized by the presence of all particles; in contrast, only part of the particles are sedimented by (standard) centrifugation used here. The amount and size of particles remaining in suspension is most likely not identical for all of the samples which explains the observed spreading in the redox potentials after centrifugation.

For sample *REF_1(II/III) c*, suspension and ultrafiltration values are very close to each other and only the centrifugation value is off by about 250 mV. In this special case an equilibrium value for the centrifugation measurement was not reached within 40 min, the measurement was stopped nevertheless. For the *REF Sus magn a* sample, the values obtained under the three different conditions are all very close to each other, varying by not more than 30 mV.

First conclusions: At first sight, the measurement in the centrifugate does not lead to an unambiguous picture and should not be taken into account for further discussions. Redox potentials measured in suspension and after ultrafiltration differ strongly from each other, but show in most cases a systematic trend (10 kD data approx. 250 mV (4.2 pe units) more positive than suspension data).

A number of points of critique of the experimental approach taken might be raised. Namely, that the aquatic species in the liquid phase are not anymore in equilibrium with the solid phase after the phase separation step by filtration; that the absence or extent of sorption effects during the ultrafiltration procedure has not been investigated and that sample oxidation due to oxygen leaking into the sample tubes during centrifugation outside of the glovebox can not be excluded. Further experiments using ultracentrifugation as a phase separation method equivalent to ultrafiltration (but without the disadvantages mentioned above) could help in evaluating the obtained data. Also, to establish comparability between suspension samples and centrifuged samples, the centrifuge used should imperatively be placed inside the glovebox.

Appendix 1 –Instruments and equipement used:

Electrodes and pe-pH meter used:
Redox electrode: Pt-combination electrode, Methrom, 6.0451.100, Ag/AgCl reference electrode, 3 M KCl filling solution. pH electrode: Thermo-scientific Orion 8103 SC Ross Semi-Micro Combination pH electrode. Both electrodes were connected to an Orion pe-pH-meter (model 720A) via BNC-connectors.

Spectro-photometer: Carl Zeiss Jena, composed of components NMC 105, CLH 500, MCS 501 UV-NIR; run with Aspect Plus software, version 1.73 © 1993-2002.

For ultrafiltration: Microsep 10k Omega filters, P/N OD 010C45, Lot: 07550960.

Chemicals:
Ferrospectral: Merck, 1.11616.0001, Lot 735113.
NH_4Ac - Ammoniumacetate: Merck, Fractopur, 1.16103.1000, charge A379203 303.
NH_2OH HCl - Hydroxylammonium chloride: Merck, p.a., 1.04616.0100, charge A 250116042. (Fe max 0.0005%).
Fe ICP Standard: 1000mg/L Fe, Merck, Certipur, 1.70326.0100, $Fe(NO_3)_3$ in 2-3% HNO_3. 1L = 1.015 kg, NIST SRM r ckf hrbar.

ReCosy, Intercomparison Exercise

Within Workpackage 2 “Development of redox determination methods”

Redox Measurements of Saline Samples by Spectrophotometric and Potentiometric Methods

Barbara Bischofer, Tina Scharge and Sven Hagemann

Short Description

a) Determination of Redox Potential by Standard Pt-ring Electrode and Correction for Salinity

b) Determination of Fe-specific Redox Potential by UV/VIS-Spectrometry

c) Comparison of Both Methods

d) Comparison with other Groups

Background and Objectives

The reliable prediction or the correct measurement of the redox value is a fundamental requirement e.g. for the calculation of the arising heavy metal and radio nuclide concentration of an underground disposal in case of hydrological incidents. But one basic condition for the measurement of redox values is not valid for saline solutions: a low ionic strength of the solution. In saline solutions redox measurements are biased because of incalculable liquid junction potentials at the reference electrode.

In answer to these challenges two methods were developed for the conversion of primary measuring data into a “calculated Pt-redox potential for an ionic strength of zero”.
Within the first method a redox measurement is conducted by a standard Pt ring electrode and a subsequent correction for the salinity according to the different ion concentration of Na^+, Mg^{2+}, Ca^{2+}, K^+, SO_4^{2-} and Cl^-.
The second method is based on the assumption that Fe^{II} and Fe^{III} compounds contribute most significantly to the measured potential at the Pt electrode because of the fast and reversible Fe^{II}/Fe^{III} redox equilibrium as well as of the omnipresent existence of the Fe^{II}/Fe^{III} redox couple in natural solutions. Reliable determinations of the redox state of saline solutions will be undertaken by measuring the Fe^{II}/Fe^{III} -ratio and -species by UV/VIS spectrometry. The subsequent calculation of the Fe-specific redox potential for an ionic strength of zero is

carried out via modelling of the activities for Fe^{2+} and Fe^{3+} in solution and a correction for the salt ion concentration.

Experimental method and approach

For the measurement of the redox potential with the standard platinum ring electrode (Metrohm 6.0451.100), an aliquot of the solution was filtrated in the Ar glove box into a closed titration vessel. Outside the Ar glove box, Ar was permanently induced into the vessel through a little opening to preclude any oxygen. The redox electrode as well as a pH electrode and a temperature sensor were inserted into the vessel. Before inserting, electrodes were rinsed with distilled water and carefully patted dry with a tissue. Now, the solution was stirred for 20 minutes and afterwards left 5 minutes at rest prior to any reading. Readings were done at regular intervals (5 min or longer) until stability. Reading was taken as stable if the drift was not more than 0.1 mV/min. The performance of the redox electrode was checked back home and the readings corrected for.

A hypothetical redox potential Rx_0 at zero ionic strength was defined on the basis of the mixed activities of $FeCl_2$ and $FeCl_3$:

$$Rx_0 = E^0 - 0{,}059 \log \frac{a_{Fe^{2+}} a_{Cl^-}^2}{a_{Fe^{3+}} a_{Cl^-}^3}$$

In solutions of higher ionic strength the apparent redox potential E (which is the measured redox potential) differs from Rx_0 by ΔRx, a term that expresses the effects of the medium concentration on the half cell potential of the redox electrode:

$$E = Rx_0 + \Delta Rx = E^0 + \Delta Rx - 0{,}059 \log \frac{a_{Fe^{++}} a_{Cl^-}^2}{a_{Fe^{+++}} a_{Cl^-}^3}$$

A function for ΔRx can be derived by measuring the apparent redox potential E in solutions of known redox potential Rx_0. In the case of a NaCl-solution ($c_{NaCl} > 0{,}1$ mol/kg) Rx_0 can be calculated by the following formula:

$$Rx_0 = E + 0.07048 + 0.06470 \log c(\mathrm{NaCl})$$

For the pH measurements, carried out with a Ross Electrode, a three point calibration with buffers at pH 2, pH 4 and pH 7 were done every day prior to measurements. For saline solutions, the measured apparent pH_{app} was corrected for salinity by applying a medium dependend term ΔpH to give the negative logarithm of the hydrogen (H^+) concentration $p_cH = \Delta pH + pH_{app}$.

For the determination of the redox potential by spectrophotometry Fe^{II} and total iron concentration are determined according to the “German standard methods for the examination of water, waste water and slugde; cations (group E); determination of iron (E1)”. A defined amount of sample, buffer solution, phenanthroline solution and additionally reducing agent in case of total iron determination are put into 10 ml and 50 ml volumetric flask, respectively and filled up with Milli-Q water (18.3MΩ). After a waiting period of at least 15 minutes the UV/VIS-spectrum is recorded between 800 and 300 nm with a Varian Cary 5000 spectrophotometer using 1cm and 10cm cuvettes, respectively. For iron concentrations below 0.01 mg/l the UV/VIS-spectra are measured with a S2000 fiber optic spectrophotometer coupled with a 1 m Longpass Flow Cell. Here the samples are prepared in 25 ml volumetric PMP flasks, which are purified by HCl leaching to preclude interfering impurities. Samples have also to be filtered before inserted into the flow cell to avoid particle infiltration. Independent of the path length in the flow cell, the iron concentration is calculated through a 3 to 5 point calibration which is recorded immediately before the samples. Afterwards the activities of Fe^{II} and Fe^{III} are calculated using the concentrations of the main anions and cations in solution and EQ3/6 as a modeling tool with Pitzer ion interaction parameters from recent GRS reports. Additionally a model, also developed by GRS, was applied that accounts for the formation of hydroxo complexes in saline solutions. Using the activities for Fe^{2+}, Fe^{3+}, and Cl^- obtained by these calculations, the corrected redox potential for an ionic strength of zero (Rx_0) is computed according to:

$$Rx_0 = E^0 - 0{,}059 \log \frac{a_{Fe^{2+}} a_{Cl^-}^2}{a_{Fe^{3+}} a_{Cl^-}^3}$$

The measured redox potential in saline solutions (= apparent redox potential) E is obtained by addition of ΔRx ($E = Rx_0 + \Delta Rx$).

Solutions measured

There are five solutions measured by GRS, namely:

a. REF 1 (II/III) c: solution of 0,1 mol/l NaCl with $FeCl_2$ and $FeCl_3$, ratio 1:4, total Fe concentration $5*10^{-4}$ mol/l, p_cH ~ 2, adjusted with HCl

b. REF 2 Na c: solution of 5,0 mol/l NaCl, Fe(II) and Fe(III) chloride $1*10^{-4}$ mol/l each, p_cH ~2, adjusted with HCl

c. REF 2 Mg c: solution of 4,5 mol/l $MgCl_2$, Fe(II)- and Fe(III) chloride $1*10^{-4}$ mol/l each, p_cH ~2, adjusted with HCl

d. REF 2 Ca c: solution of 2,0 mol/l $CaCl_2$, Fe(II)- and Fe(III) chloride $1*10^{-4}$ mol/l each, p_cH ~2, adjusted with HCl

e. NAT 4: IP21 solution (Mg rich high salinity brine), diluted by 10 vol% and additionally spiked with Fe(II) and Fe(III) chloride, adjusted with HCl to pH ~2.

Outcome of the study

Table 1 shows the results of pH and Eh measurements as well as the conversion to p_cH and Rx_0h[1]. The p_cH of the measured solution are all between 2.2 and 2.5.

The results for the two redox measurements correspond very well. The Eh values derived by the two independent methods differ only by 17 mV at maximum. The good consistency of the Rx_0h values suggests that both methods give reliable results. Eh and Rx_0h differ significantly in the saline samples (95 to 120 mV for REF2/ NAT4) which underlines that in saline solutions measured Eh are misleading (appearing less oxidizing) if not corrected for medium effects.

Table 1: Results of pH and Eh measurements and conversion to p_cH and Rx_0h [1]

Sample	**Hydrogen (H^+) concentration/ activity**		**Redox potential results obtained with Pt ring electrode**		**Redox potential results obtained with UV/VIS spectrometry**	
	pH_{app}	**p_cH**	**Eh [mV]**	**Rx_0h [mV]**	**Eh [mV]**	**Rx_0h [mV]**
REF 1 (II/III)c	2.52	2.23	714.0	720.2	704.8	711.0
REF 2 Na c	1.38	2.22	702.4	821.1	691.9	810.6
REF 2 Mg c	-0.34	2.29	692.3	794.7	675.7	778.1
REF 2 Ca c	1.56	2.37	710.2	789.9	713.2	793.0
NAT 4	0.50	2.50	685.6	780.4	672.9	767.8

Comparison and Discussion

GRS was especially interested in the acidified and saline samples, namely REF 1 (II/III) c, REF 2 Na c, REF 2 Mg c, REF 2 Ca c and NAT 4. While the ionic strength of sample REF 1 (II/III) c was only 0.1 mol/l, the ionic strength of the other samples was between 5 and 15 mol/kg. All REF 2 samples contained $2 \cdot 10^{-4}$ mol/l Fe with Fe(II)/Fe(III)=1. REF 1 (II/III) contained $5 \cdot 10^{-4}$ mol/l Fe with Fe(II)/Fe(III)=1/4. In case of NAT 4 the iron concentration was unknown but expected to be in the same order of magnitude. Due to acidification to approximately pH 2, a relatively large amount of Fe(III) was in solution. Thus, a short equilibration time and a stable signal were expected. The results of the different participants and their methods are compared in table 2. It can be seen that the readings are close together. The standard deviation is small with regard to measurements of other reference and natural samples at the ICE.
But how meaningful are these readings in view of the oxidation state determination of the redox active species? Potentiometric measurements in saline solutions are hampered, because of the variable liquid junction potential at the reference electrode. For this reason the measured potential has to be corrected before conclusions about the redox state can be drawn.

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[1] Rx_0h is the hypothetical redox potential measured with a standard hydrogen electrode instead of a Ag|AgCl|KCl(3 M). Therefore $Rx_0h=Rx_0 + E_{Ref} = Rx_0 + 0{,}207V$

Correction functions for Fe(II)/Fe(III) in the binary systems NaCl, KCl, $MgCl_2$, and K_2SO_4 are given in Scharge et al. 2010. For different background salts or complex solutions approximations have to be used.

Table 2: Comparison of Eh data given in mV for saline samples. Values in italics are not included in the calculation of mean value and standard deviation.

Group	**REF 1 (II/III) c Eh [mV]**	**REF 2 Na c Eh [mV]**	**REF 2 Mg c Eh [mV]**	**REF 2 Ca c Eh [mV]**	**NAT 4 Eh [mV]**
GRS Eh uncorr.	714	702	692	710	686
GRS UV uncorr.	705	692	676	713	673
BGRM Pt	697	690	677	697	
BGRM Au	647	666	672	694	
BGRM C	688	683	685	689	
CNRS Pot.	704				
CNRS Amp.	694				
FZD ITU	698				
ITU Pt	710				
ITU Au	698				
PSI	694				*575*
Amphos					666
FZD ITU					674
INE_CW					648
MSU, INE					659
ULOU					*292*
Mean value	**695**	**687**	**680**	**701**	**668**
Standard deviation	**18**	**13**	**8**	**10**	**13**

The necessity of the correction function will be pointed up using the example of sample REF 2 Mg c. With UV-spectrometry we could analyze a Fe(II)/Fe(III)-ratio of 1.1/1. The mean value of the readings, 680 mV, leads to an activity ratio of 34/1 using the Nernst equation. The corrected redox value calculated with the correction functions given in Scharge et al. (2010) is 776 mV (a difference of 96 mV) and this leads to 0.8/1. The difference between measured and corrected potential results on the one hand from the variable liquid junction potential and on the other hand from the complexation of Fe(III) with chloride. We are not able to make a statement about the more determining factor but it is obvious that correction functions have to be used to calculate the concentration ratio of redox species in saline solutions. The correct ratio of the redox sensitive species is important e. g. for geochemical modeling.

Even in REF 1 (II/III) c an eight times higher activity ratio is calculated from the potentiometric measurement compared to the UV-spectrophotometric analyzed concentration ratio. In this case not the liquid junction potential but the complexation of Fe(III) with chloride is probably the main reason for the difference in activity and concentration. In case of complexation the correction functions are even at this low ionic strength of 0.1 mol/l helpful to determine the concentration ratio of Fe(II) and Fe(III).

GRS investigated also the natural samples NAT 1 b, NAT 2, and NAT 3. With potentiometric measurements a stable signal was observed after 90 min for NAT 1 b. In case of the other two samples the signal drifted remarkably even after two hours. The UV-spectrophotometric analysis showed that the iron concentration was below the detection limit of $1 \cdot 10^{-7}$ mol/l for these three samples. Neither iodine nor selenium as an origin for alternative redox couples could be detected by other participants of the ICE. That raises the question if any redox couple was present in these samples which could induce a detectable current on the electrode surface.

The important conclusion of the ICE for GRS is that redox measurements on its own are not sufficient for a reliable statement about the redox state. They have to be supported by quantitative analysis and thermodynamic evaluation. The analysis of the redox sensitive species is necessary to secure whether they exist in significant concentrations. Further more, the concentration of the background ions in saline solutions have to be determined to correct a possible bias induced by a variable liquid junction potential.

Reference: Scharge, T., Bischofer B. P., Hagemann S., Schönwiese D. (2010): Spectrophotometric and potentiometric determination of the redox potential in solutions of high ionic strength, KIT Scientific Reports 7557, 2010, 147-159.

Institute of Physics, G. Lujaniene

Redox potential (room temperature, Ar atmosphere)
Samples were measured using a WTW SenTix ORP electrode and a WTW inoLab Multi Level 1 meter. Drifts in the measured potential were less than 1-2mV between the readings after 10 minutes.

Measured sample	mV	Equilibrium reached, min	Comments
RH 28, WTW	221		
REF1(II/III)a	188.0±0.4	40	strong drift
REF4 ACW2	-984±1	12	
REF3 HCa	114.2 0.3	31	
REF3I Se a	-39.9 0.3	46	strong drift
RH 28, WTW	221		
RH 28, WTW	226		
REF4 ACW1	-912 1	10	
REF1 Fe b	-240 1	10	
RH 28, WTW	225		
RH 28, WTW	225		
NAT1a	118.7 0.3	47	strong drift
NAT2	100.8 0.3	24	
NAT3	61.4 0.3	30	strong drift
RH 28, WTW	223		

InterCompEx

ReCosy, Intercomparison Exercise

Within Workpackage 2 “Development of redox determination methods”

Short summary description

KIT-INE (1): Separation of drift on reference and active electrode

Florian Huber, Nikolaus Müller and Gunnar Buckau

Background and Objectives

Measurement of the redox potential of natural aquatic systems by redox active electrodes frequently shows drift over extended periods of time. This drift may have different reasons, including:

i. Slow transformation of the active electrode material surface by, for example formation of sulphides, slow removal of oxidized or reduced material from previous contact with solutions containing such material,

ii. Deposition of material on the active electrode surface gradually converting the active electrode to one of the deposited material,

iii. Leakage into or out through the reference electrode liquid junction resulting in a different reference system potential,

iv. Chemical conversion of the reference electrode glass surface by long contact time with the measured solution, or

v. Catalytic conversion of the measured solution by reactions with the active electrode surface material, resulting in a shift of the redox potential of the solution.

The present study aims at separating the impact from point “iii” from the other ones as they may occur during long redox value measurements. The present study also avoids different catalytic conversion of a specific solution through contact with different active electrode materials. Thus, the objectives of the present study is to (a) decouple the potential drift in measurement through exchange of liquid between the reference electrode system and the studied water sample, (b) avoid different pace of chemical conversion of the measured solution by contact with different active electrode materials, (c) draw conclusions on the potential magnitude of such an impacts on the redox measurements, and (d), if adequate, provide recommendations on how to avoid such an artefact.

Experimental method and approach

Three different single electrodes are used in this study, namely Pt, Au and glassy carbon (CG) which are coupled to the same Ag/AgCl reference electrode (3M KCL filling solution) for measurements. The redox potential of different samples is measured by leaving the active electrodes in the solutions for at least some 12 to 24 hours. In the case of Grimsel groundwater (NAT 3) measurements at longer time scales have been conducted. At different points in time, more frequently at the beginning of the measurement of a specific solution, the reference electrode is introduced and the potential against the active electrodes is registered. Between the measurements, the reference electrode is stored in 3 M KCl. By this approach, the reference electrode is not subject to slow drift through contact with the solution and its chemical components, and also not by exchange of liquid between the reference system and the liquid measured.

The active electrodes are left in clean water prior to the start of the study. They are not subject to particular pre-treatment between the studies of different solutions, except for flushing with clean water.

Measurements are conducted in Ar inertgas box, with oxygen contamination of solutions and equipment avoided by standard lab procedures for work under anoxic conditions.

There is no control of temperature. The measurements are conducted in room temperature. Furthermore, pH of the solutions has not been measured.

The electrodes are checked for their function by Eh buffer prior to, and after the study, unless specific reasons are given.

Solutions measured

There are four solutions measured, namely:

a. NAT 1a, Gorleben Soft Humic Rich Groundwater, S102-2227 (RCM 80), Conditioned in a fridge since 03.07.1991

b. NAT 1b, Gorleben, Deep Channel Brine, S218-944 (RCM 91), Conditioned in a fridge since 02.12.1993

c. NAT 3, Grimsel Groundwater, Granitic, very low content of dissolved species.

Expected outcome

Prior to the study, it is expected that the active electrodes will show drift, but less than when the drift from the reference system is taking place simultaneously. It is furthermore expected that one can identify the relevance of different paces of chemical conversion in contact with the different active electrode materials. The latter should be possible, especially by comparison with other measurements with the three different active electrode materials.

Outcome of the study

Results of the Eh measurements as function of time for all 3 examined solutions are listed in Table 1 and depicted in Figure 1.

NAT 1a

For 2 (Pt and CG) of the 3 electrodes used, satisfactory correlation within 10 to 15 mV was observed during the whole experimental duration. In contrast, Au electrode showed a deviation of ~ 80 to 90 mV compared to Pt and CG electrodes during the first 15 min. As function of time all 3 electrodes display the same trend to lower Eh values converging to values of ~ 135 mV, ~165 mV and ~ 178 mV for Au, Pt and CG, respectively at the end of the measurements. Here the deviation decreases to ~ 50mV between the Au electrode compared to Pt and CG. Long term measurements have been conducted from 960 min to 1020 min examining if Eh values reached equilibrium conditions. The drift decreases progressively towards long contact times and thus one may expect that the system is approaching equilibrium.

NAT 1b

Similar to the NAT 1a series, 2 of the 3 electrodes correlate to a great extent differing only about ~ 20-30 mV during the complete experimental duration of about 22 h. Here, in contrast to the NAT 1a measurements, the Au and CG electrodes are in good agreement while the Pt electrode shows values ~ 100mV above the ones for the 2 other electrodes. Overall, all 3 electrodes behave similar concerning the qualitatively drift to higher values. Equilibrium conditions after 22 h have not been reached, except in case of the Pt electrode showing only a small residual drift.

Nat 3

Pt and Au electrodes behave quite similar in a qualitatively way regarding the long term drift. Both electrodes start with rising potentials and then turning around after ~20h drifting to negative Eh values at the end of the experiments in contrast to the CG electrode which decrease from the beginning to the end after 140 h. The maximum difference after 20 h between all 3 electrodes applied is ~ 150 mV, which diminishes after 140 h to about ~ 60 mV. After 22 h all 3 electrode still show drift towards negative Eh values.

Regarding the very low mineralization of the Grimsel groundwater (Huber et al., 2009) (especially the Fe^{2+}/Fe^{3+} concentrations are probably below 10^{-6} M. It has been proposed, that systems where the redox couples have such low concentrations, the redox potential cannot be reliably determined (Grenthe et al., 1992)). The present system seems to qualify for this situation, i.e. the concentration of redox determining couples is too small to yield a stable signal measurable by the electrodes. Thus, the absence of redox equilibrium conditions even after 140 h is not further surprising.

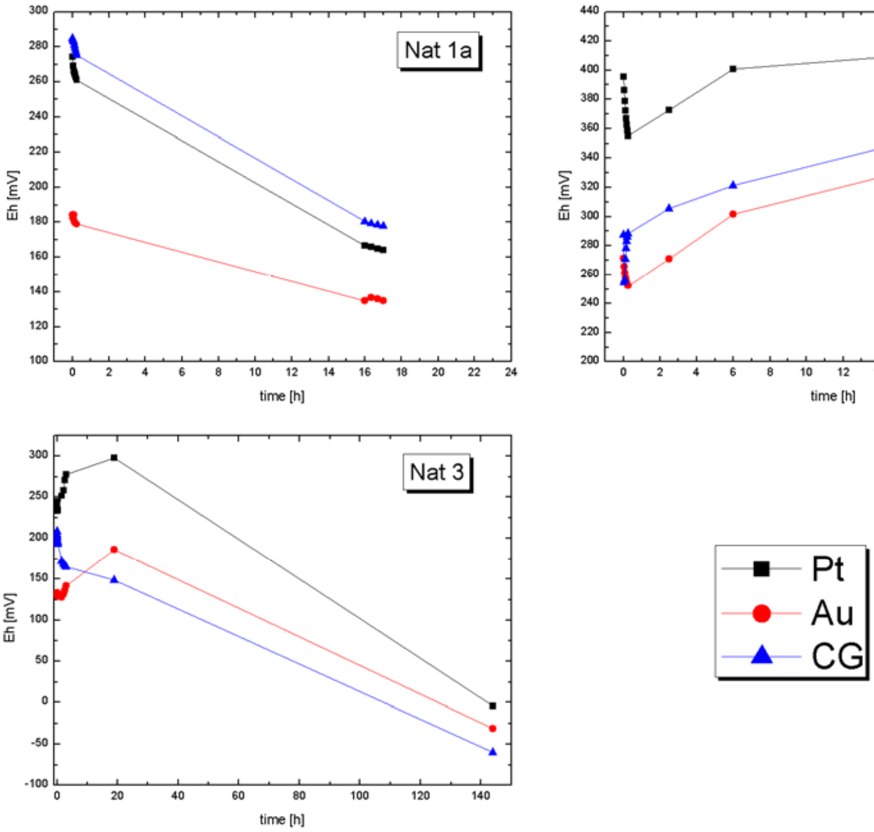


Figure 1: Upper left: Gorleben Humic Rich Ground Water (NAT 1a); Upper right: Gorleben Deep Channel Brine (NAT 1b); Lower left: Grimsel Ground Water in contact with Grimsel Fracture Filling Material (NAT3).

Table1: Experimentally determined Eh values for 3 natural groundwater samples.

	NAT 1a				**NAT 1b**				**NAT 3**		
	(Gorleben Soft Humic Rich GW)				(Gorleben Deep Channel Brine)				(Grimsel GW with FFM)		
	Pt	Au	CG		Pt	Au	CG		Pt	Au	CG
Time [min]		Eh [mV]		Time [min]		Eh [mV]		Time [min]		Eh [mV]	
1	274,1	184,3	284,8	1	395,6	271,4	287,2	1	245,1	133	208,9
3	269,2	182,3	283,8	3	386,3	265,8	254,9	3	237,4	131,7	205,1
5	266,2	184,5	282,8	5	378,6	261,4	256,6	5	234,9	131	202,4
7	265,3	180,5	281,3	7	372,3	258,4	270,8	7	234	130,5	200,3
9	264,2	179,7	279,7	9	367	256,2	278,3	9	233,7	130	198,3
11	263,1	179,5	278,3	11	362,5	254,3	283,1	11	233,8	129,5	196,3
13	262,2	179,3	276,9	13	358,7	253	286,1	13	233,9	129	195
15	261,4	179,1	275,2	15	355,3	252	288,4	15	234,2	128,6	193,6
960	166,7	134,8	180,6	150	372,7	271	305,5	90	252,2	128	172,4
980	166,1	136,5	179,3	360	401	301,7	321,1	128	259,1	131,5	168,6
1000	164,9	135,8	178,5	1260	415,5	349	368,6	159	271,1	136	166,3
1020	164,3	134,9	177,8	1280	414,7	351	372	183	278,1	141,5	165
				1300	415,7	353	376,7	1135	298,1	186,7	148,6
				1344	417,1	357,1	384,8	8640	-4,2	-31,4	-59,7

Preliminary conclusions

- Long term measurements (> 24 h) are required to reach “satisfactory agreement” (difference < 50 mV) between the 3 electrodes used (at least in the case of the 3 different measured solutions within in this study).
- The different active materials drift in comparable directions.
- The slow drift is not associated with the reference system. Keeping the reference system out of solution between measurements does not diminish the slow drift.
- The nature of the slow drift can not be resolved.

References

Huber et al. (2009). *Sorption reversibility studies on the interaction of radionuclides with FEBEX bentonite colloids/nanoparticles under Grimsel groundwater in the presence of fracture filling material.* (In preparation).

Grenthe et al. (1992). *Redox potentials and redox reactions in deep groundwater systems.* Chemical Geology 98, p.131-150.

Appendix

Redox electrodes applied:

- **Methrom** separate Pt-ring electrode
- **Metrohm** separate Au-ring electrode
- **Radiometer analytical** glassy carbon electrode (M291C-9)
- **Metrohm** Ag/AgCl reference electrode (3M KCL)

pH-Meter:

- **WTW** pH meter 720

InterCompEx

ReCosy, Intercomparison Exercise

Within Workpackage 2 “Development of redox determination methods”

Short summary description

KIT-INE (1): Separation of drift on reference and active electrode

Mirek Icker, Clemens Walther

Background and Objectives

Measurement of the redox potential by redox active electrodes frequently shows drift over extended periods or experience instabilities. One possible reason due to the very low currents flowing to the readout unit is the lack of proper signal shielding, inductive coupling by magnetic stray fields or simply excessive cable lengths. In order to overcome this problem a low cost home built impedance converter was built and introduced between electrodes and readout unit/multimeter. The setup was tested against a commercial readout unit (Orion) and a commercial impedance converter (Femto). We used a combined Pt ring electrode (Pt-Ringelektrode Metrohm: 6.0451.100.) and a couple of single electrodes (Pt wire vs Ag/AgCl micro electrode (KSI Meinsberg).

Experimental method and approach

The redox potential of different samples is measured by leaving the active electrodes in the solutions for typically 3 hours, in one case for up to 72 hours. At different points in time, more frequently at the beginning of the measurement of a specific solution, potential against the active electrodes is registered. The active electrodes are left in 3m KCl (KSI) and dilute KCl (Metrohm) prior to the start of the study. In the case of REF1 the electrodes were rinsed with MQ water and dried with a dust-free tissue after measurement. In case of the natural samples the electrodes were rinsed in turns with dilute HCl and water and thoroughly dried with a dust free slightly abrasive tissue.

Measurements are conducted in an Ar inert gas box, with oxygen contamination of solutions and equipment avoided by standard lab procedures for work under anoxic conditions.

There is no control of temperature. The measurements are conducted in room temperature.

The electrodes are checked for their function by Eh buffer prior to the measurements.

Solutions measured

The following solutions were measured, namely:

a. REF 1 Fe II/III a, Redox control by Fe powder, ~100 mg/L, pH not buffered (~9)

b. REF 1 c

c. NAT 1a, Gorleben Soft Humic Rich Groundwater, S102-2227 (RCM 80), Conditioned in a fridge since 03.07.1991

d. NAT 1b, Gorleben, Deep Channel Brine, S218-944 (RCM 91), Conditioned in a fridge since 02.12.1993

e. NAT 3, Grimsel Groundwater, Granitic, very low content of dissolved species

f. NAT 4 High salinity / brine conditions
Magnesium rich high salinity brine (IP21 Solution), 10% dilution factor

Expected outcome

The signal amplified by the impedance converter should be more robust against unwanted coupling. Due to the very low input current required <1pA, a shorter period for reaching equilibrium was expected

Outcome of the study

Indeed high stability and no influence of cable length or feed through after amplifier. However, amplifier has no influence on equilibrium which is governed by electrodes.

Preliminary results for sample are given in the table below. However, in some cases we observed pronounced changes with time which will be discussed in the full report.

Sample	Ringelectrode	Single electrodes
Ref1a II/III	309,1 mV	402 mV
Ref 1c II/III	677,2 mV	677,2 mV
Nat 1a	242,3 mV	196 mV
Nat 1 a (72h)	73,3 mV	-
Nat 1b	325,4 mV	559,7 mV
Nat 1b 2	-	164,4 mV (viel längere Messzeit als Nat 1b)
Nat 2	273,7 mV	-
Nat 3	-	244,7 mV
Nat 4	648,2 mV	-

*measured Values + correction offste of 187,2 mV

InterCompEx

ReCosy, Intercomparison Exercise

Within Workpackage 2 “Development of redox determination methods”

Short summary description

KIT-INE (1): Test of cleaning protocols for (Pt) combination electrodes

Vladimir Petrov, Melanie Böttle and Marcus Altmaier

Background and Objectives

Measured redox potential can be dependent on the state of surface of redox active electrode. The state of this surface is dependent on the method of pretreatment or cleaning. Different scientific groups use different cleaning protocols. Some of them are:

- Not use any pretreatment or cleaning protocol
- Normal exposure: rinsing with water, in case of strong contamination: cleaning the metal ring by wet paper
- The redox electrode surfaces are polished before use with diamond paste or SiO_2
- Mechanical cleaning with toothpaste followed by chemical cleaning (soak in diluted HCl)
- Polishing of Pt-surface with Al_2O_3 paste or toothpaste, HCl cleaning of diaphragm
- Immersing in fairly strong (~0,1 M) HCl, polishing with tissue paper
- Cleaning with HCl and degreasing with ethanol
- Cleaning with oxidizing acids
- Immersing electrode in nitric acids (1:1 H_2O) for about 30 minutes, allow it to cool, rinse with water afterwards
- Pt electrodes need to be pretreated with warm HNO_3 and acetone and rinsed by MQ water sufficiently
- Use of sulphochromic mixture and if necessary of “Brillo Pad”
- Multi-step scheme: 1. Alcohol (methyl, ethyl or isopropyl); 2. Ammonium hydroxide, NH_4OH, concentrated; 3. Mixed acid cleaner: mix concentrated H_2SO_4 and HNO_3 in 2:1 ratio
- In general, modest current flows. Experimented with molten KNO_2
- Ascorbic acid, storage in KCl

The aims of a present study are to see how different cleaning protocols affect the measured redox potentials or response times and to systematize approaches.

The following representative protocols have been tested:

Protocol #1: Rinsing with MQ water

Protocol #2: Immersing in fairly strong (~0,1 M) HCl, polishing with tissue paper

Protocol #3: Mechanical cleaning, wiping of electrode before use with SiO_2. Rinsing with MQ water

Protocol #4: Multi-step scheme: 1. Alcohol (methyl, ethyl or isopropyl); 2. Ammonium hydroxide, NH_4OH, concentrated; 3. Mixed acid cleaner: mix concentrated H_2SO_4 and HNO_3 in 2:1 ratio

Experimental method and approach

Before every redox measurement each of four Pt combined electrodes is cleaned using one of the protocols. Measurements are conducted in Ar glove box, with oxygen contamination of solutions and equipment avoided by standard lab procedures for work under anoxic conditions. The redox potential of different samples is measured by immersing the Pt combined electrodes in the solutions for about 24 hours without stirring. At different time intervals, more frequently at the beginning of the measurement of a specific solution, the potential of each electrode is registered. Final Eh values are used for calculation of pe:

$pe = -\log[e^-] = Eh\frac{F}{RT\ln 10}$, at 25°C $pe = 16.9Eh$.

There is no control of temperature. The measurements are conducted in room temperature.

The electrodes are checked for their function by Eh buffer (220 mV vs. Ag/AgCl) prior to, and after the study, unless specific reasons are given.

The pH of all the samples are measured after the Eh measurement by combination glass electrodes calibrated against pH standard buffer.

Solutions measured

There are five solutions measured:

a. REF 1 Fe a, Redox control by Fe powder, ~100 mg/L, pH not buffered (~9).

b. NAT 1a, Gorleben Soft Humic Rich Groundwater, S102-2227 (RCM 80), Conditioned in a fridge since 03.07.1991.

c. MIC 1, sample with microbial activity.

d. NAT 3, Grimsel Groundwater, Granitic, very low content of dissolved species.

e. NAT 4, high salinity conditions.

Measurements were done in the order sample a to sample e. The cleaning steps described above were performed between each measurement of the samples.

Expected outcome

It is well known that coatings or surface alterations of Pt redox sensors occur, leading to biased measurements. Therefore, it can be expected that if different electrodes are cleaned by using different protocols, they record different redox potentials and different response times. It is further expected that a possible coating should reflect the conditions of the last measured sample. If the cleaning had no effect it would be expected to record the same potential with all four different electrodes used.

Outcome of the study

The measurements performed during ICE on the 5 different samples are summarized below.

Sample REF 1 Fe a

In the case of sample "REF1 Fe a" all Pt combined electrodes reach the equilibrium state after ~15 hours of experiment. During the first hours, protocol #1 is was considerably lower than Protocols #2,3,4. After long equilibration times, the most similar Eh values measured by electrodes treated with protocols #1 and #4. The dependence of measured Eh values on time shown in Figure 1.

Time	Eh, mV			
	Protocol 1	Protocol 2	Protocol 3	Protocol 4
5 min.	107	312	240	271
10 min.	90	270	217	252
30 min.	28	175	224	206
1 h.	15	179	227	208
2 h.	35	213	206	175
19 h.	-277	-233	-357	-288
25 h.	-264	-216	-356	-269
pe	-4,5	-3,6	-6,0	-4,5
pH	9,1	9,0	9,0	9,1
pe+pH	4,6	5,3	3,0	4,6

average Eh = -280 60 mV

average (pe+pH) = 4,4 1

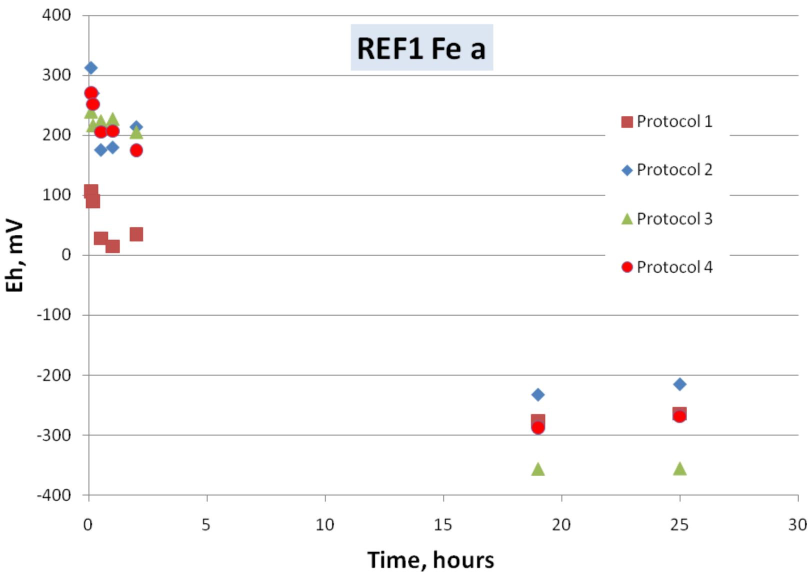


Figure 1. Dependence of Eh values of sample "REF1 Fe a" on time measured by Pt combined electrodes treated with different cleaning protocols.

Sample Nat 1a

In the case of sample “Nat 1a” all the four differently treated Pt combined electrodes do not reach stable reading even after 1 day of experiment. Again the behaviour after short equilibration times is markedly different. The most similar Eh values measured by electrodes treated with protocols #2 and #4. Protocol #3 is about 50mV, Protocol #1 about 100mv above the level of #2 and #4. The dependence of measured Eh values on time shown in Figure 2.

Time	Eh, mV			
	Protocol 1	Protocol 2	Protocol 3	Protocol 4
5 min.	399	282	226	333
10 min.	408	299	296	331
30 min.	416	320	347	344
1 h.	418	335	371	348
2 h.	419	344	384	358
17 h.	398	321	366	316
23 h.	388	298	345	301
pe	6,5	5,0	5,8	5,1
pH	8,4	8,5	8,5	8,6
pe+pH	15,0	13,5	14,3	13,7

average Eh = 330 40 mV

average (pe+pH) = 14,1 0,7

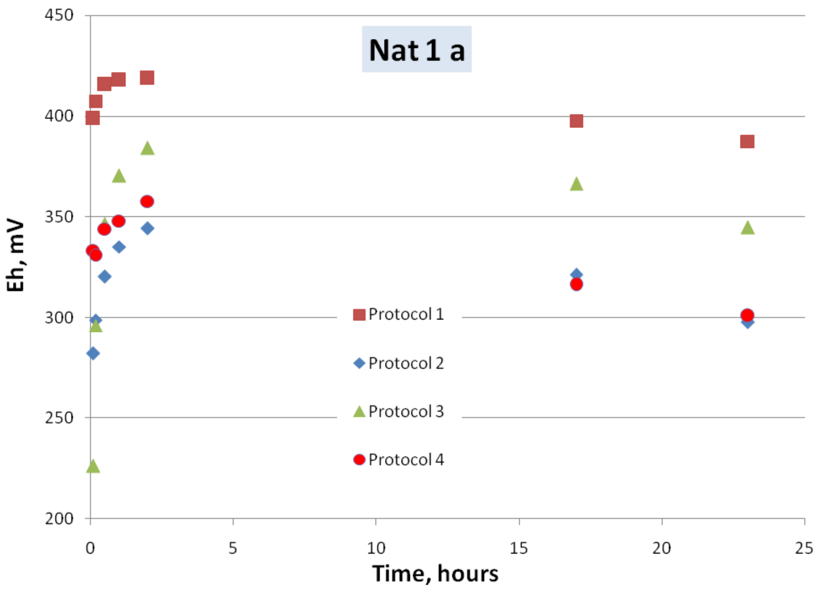


Figure 2. Dependence of Eh values of sample “Nat 1a” on time measured by Pt combined electrodes treated with different cleaning protocols.

Sample MIC 1

In the case of sample "MIC 1" all Pt combined electrodes show similar Eh values after 2 hours and from then only small drift of Eh values even after 1 day of experiment. During the first hour, however, the readings were changing quite rapidly. It is not clear why Protocol #3 is starting from very low values contrary to the trend observed for #1, #2, #4. The dependence of measured Eh values on time shown in Figure 3.

Time	Eh, mV			
	Protocol 1	Protocol 2	Protocol 3	Protocol 4
5 min.	-182	-241	-333	-236
10 min.	-196	-245	-317	-241
30 min.	-235	-251	-293	-248
1 h.	-245	-255	-278	-252
2 h.	-253	-260	-269	-257
17,5 h.	-302	-306	-303	-301
24 h.	-314	-317	-315	-311
pe	-5,3	-5,3	-5,3	-5,3
pH	7,9	8,1	7,8	7,9
pe+pH	2,6	2,8	2,5	2,7

average Eh = -314 3 mV

average (pe+pH) = 2,6 0,1

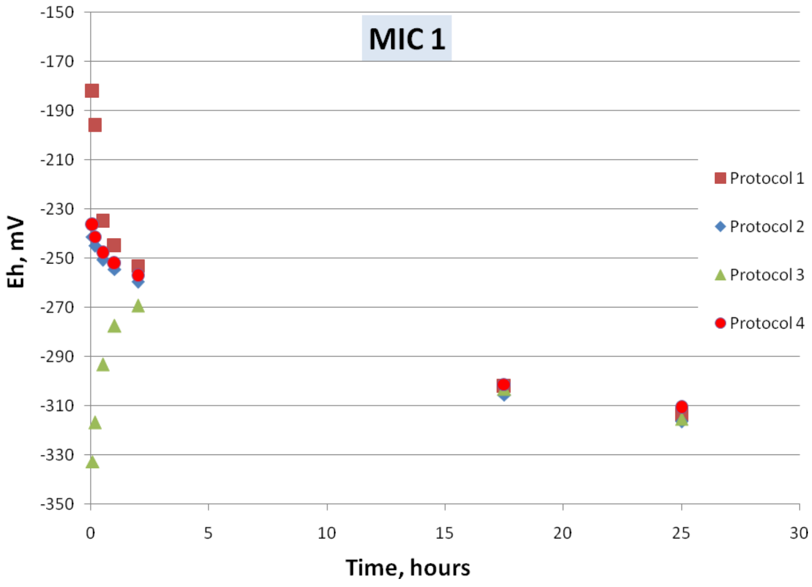


Figure 3. Dependence of Eh values of sample "MIC 1" on time measured by Pt combined electrodes treated with different cleaning protocols.

Sample NAT 3

In the case of sample "Nat 3" all four sensors show considerable drift over 24h, probably reflecting an alteration of the reference sample during measurements. Only the Pt combined electrode treated with procol #4 reaches stable conditions after 24 hours of experiment. After 20 hours, samples treated with protocol #1 and #3 are very similar, #2 and #4 being roughly 100mV or 200 mV higher. The dependence of measured Eh values on time shown in Fig. 4.

Time	Eh, mV			
	Protocol 1	Protocol 2	Protocol 3	Protocol 4
5 min.	178	125	-116	248
10 min.	160	119	-33	252
30 min.	136	110	55	257
1 h.	102	100	84	253
2 h.	66	78	82	238
18 h.	-16	97	-23	194
21 h.	-4	117	-1	217
24 h.	3	144	36	233
42h.	125	213	158	239
pe	2,1	3,6	2,7	4,0
pH	9,4	9,4	9,6	9,4
pe+pH	11,5	13,0	12,3	13,4

average Eh = 184   52 mV

average (pe+pH) = 12,6   1

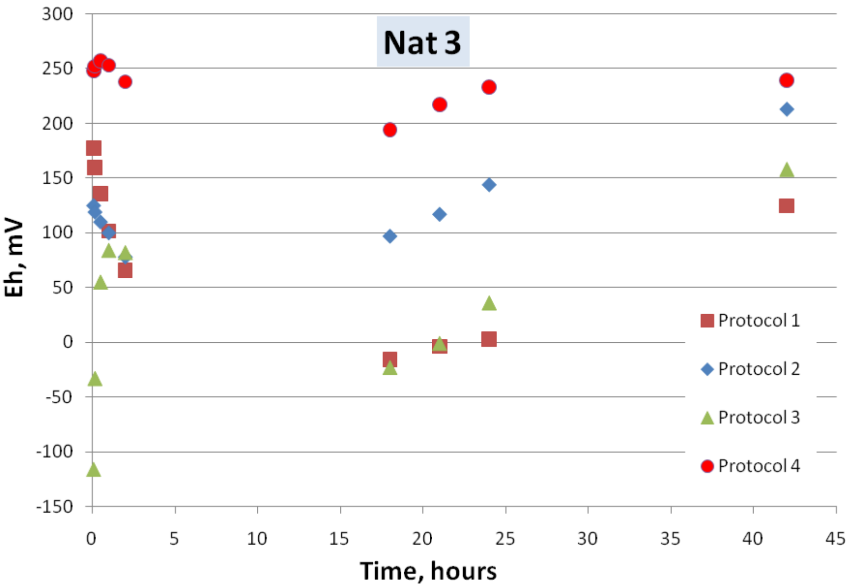


Figure 4. Dependence of Eh values of sample "Nat 3" on time measured by Pt combined electrodes treated with different cleaning protocols.

Sample NAT 4

In the case of sample “Nat 4”, the Pt combined electrode treated with the most elaborate protocol #4 reaches the equilibrium state after 30 minutes of experiment. Electrodes treated with protocols #2 reaches the equilibrium state after 2 hours, the electrodes treated with protocols #3 and #1 after about 6 hours. After 6 hours, all electrodes are very stable and show similar Eh values. It should be noted, that sample NAT 4 is quite acidic. The pH_{exp} of 0.4 given in the table is the operational value obtained for this saline sample, it does not represent a thermodynamically well defined proton activity. The dependence of measured Eh values on time shown in Figure 5.

Time	Eh, mV			
	Protocol 1	Protocol 2	Protocol 3	Protocol 4
5 min.	315	359	269	638
10 min.	336	420	310	634
30 min.	377	503	384	657
1 h.	452	599	470	661
2 h.	549	643	553	659
5 h.	642	652	611	660
22 h.	654	661	650	665
28 h.	654	661	654	665
pe	11,1	11,2	11,1	11,2
pH_{exp}	0,4	0,4	0,4	0,4
pe+pH	11,5	11,6	11,5	11,7

average Eh = 659   6 mV
average (pe+pH) = 11,6   0,1

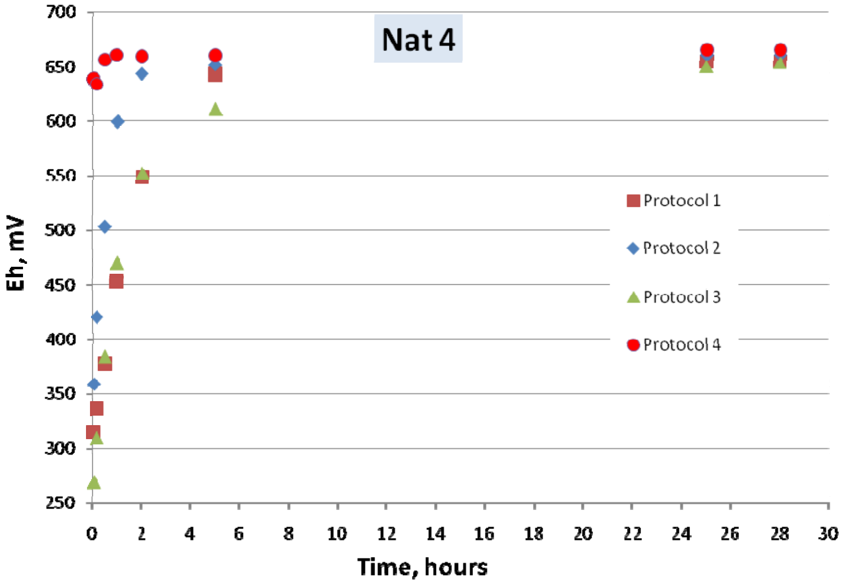


Figure 5. Dependence of Eh values of sample “Nat 4” on time measured by Pt combined electrodes treated with different cleaning protocols.

Conclusions

Measurements performed with four Pt combination electrodes using different pre-treatment protocols show no clear systematic trend, not allowing the recommendation of one preferable protocol. There was no obvious dependence of measured E_h values on the cleaning protocols used. In most cases, Pt combined electrodes treated with different cleaning protocols showed rather similar readouts or “pe+pH” values after long equilibration times. However, when looking at response times and the behaviour of sensors during the first hour of measurements, usually large differences (up to several hundred mV!) between different protocols were observed. This indicates that the different pre-treatment protocols did in fact somehow influence the electrode surface although we cannot explain or systematize this effect at present. It has also been observed, that the nature of the samples affected the response time of Eh measurements. The very long equilibration times observed are probably due to the fact that samples were not stirred during measurement.

-Recosy Intercomparison Excercise (ICE).

PSI-LES: Measurement of redox potentials in reference solutions with a combined redox electrode. Effect of measurement time. Comparison with thermodynamic calculations

Jan Tits and Xavier Gaona

1. Introduction

Oxidation – reduction transformations are among the most important factors controlling the aqueous speciation, solubility, and sorption behaviour of redox-sensitive actinides such as neptunium. Inert metal electrodes (Pt, Au) combined with a reference electrode (usually an Ag/AgCl electrode) are widely used to measure the redox potential of chemical systems. However, a quantitative interpretation of the measured redox potentials is often hindered due to a poor conceptual understanding in mainly two areas: (1) the kinetics of electron transfer reactions at the electrode surfaces and (2) the measurement and interpretation of redox potentials in natural waters containing multiple redox couples. Redox potential measurements with inert metal electrodes give only reliable values for a few redox couples characterized by fast redox reaction kinetics (e.g., Fe(II)/Fe(III), Mn(II)/Mn(IV), Np(III)/Np(IV),…). Otherwise the measured E_h value may drift according to electrokinetic phenomena, mixed potentials or impurities at the metal electrode surface. Electrode kinetics are discussed in detail in e.g., Peiffer et al. (1992), Stumm and Morgan (1996); Bard and Faulkner (2000). Different redox couples in natural waters are very rarely in equilibrium because they tend to react at different rates. Hence, an E_h value measured for one specific redox couple does not necessarily give information about the redox state of other redox couples in the same system (e.g., Grenthe et al., 1992, Stumm and Morgan, 1996, Sigg et al., 1999).

2. Objectives

The goal of the PSI study within the framework of the ICE was to evaluate the reliability and reproducibility of E_h measurements in various types of reference solutions containing different redox couples. To this aim, E_h values were measured as a function of time, using combined redox electrodes. For two series of samples (alkaline reference pore waters (MQ1, MQ2, ACW1 and ACW2) and Fe samples in dilute NaCl solutions (REF I (II/III) a and REF 1 (II/III) c), the measured E_h values were compared with E_h values obtained from thermodynamic calculations. In addition, the effect of stirring on the response time of the electrode was tested. Furthermore the measured redox potentials were compared with measured values obtained by other participants with different analytical and electrochemical methods with the aim of identifying advantages, disadvantages, and complementarities of the different methods.

2. Experimental methods

The redox potential of the samples was measured using a Metrohm combined redox electrode consisting of a Pt-ring indicator electrode and a Ag/AgCl reference electrode. All reference samples were measured by immersing the electrode in the solution for 10 minutes. Some samples were measured over longer periods of time (up to 90 minutes). Redox values were recorded after 1 minute, 5 minutes, 10 minutes and in some cases, 60 or 90 minutes. All reference samples were stirred during the redox measurement. Only the redox potential of hyperalkaline reference samples was measured without stirring to allow an evaluation of the effect of stirring on the electrode response time. After the redox measurements, the proper functioning of the electrode was checked with a redox standard (Metrohm) having a redox potential of +243 mV at 25°C.

In addition to the redox potential the pH of each solution was measured. The read-out was accepted when the pH drift was less than 0.05 pH units per minute prior to the pH measurements.

3. Samples measured

3.1. Alkaline solutions

Four hyperalkaline pore water samples have been provided by PSI for the Recosy ICE. They cover the pH range relevant for cementitious environments ($10.0 < pH < 13.3$). The pore water compositions and pH were fixed by equilibration of MilliQ water (MQ1 and MQ2) or artificial cement pore water (ACW1 and ACW2) with C-S-H phases with different $CaO:SiO_2$ ratios. ACW is a NaOH and KOH rich pore water ([Na]=0.11 M, [K] = 0.18 M and pH = 13.3) corresponding to a cement pore water in equilibrium with a fresh hardened cement paste. A reducing redox potential was obtained by the addition of $5 \cdot 10^{-3}$ M Na-dithionite. In the presence of this reducing agent, it was empirically observed that the redox potential is defined by the lower stability limit of H_2O (i.e. the reduction of H_2O to H_2). The underlying reason for this behaviour and for the validity of the measured E_h as a redox reference is currently not understood.

The four alkaline reference porewaters were prepared as follows:

Aerosil 300 and CaO powders were mixed in Teflon bottles to give $CaO:SiO_2$ weight ratios of 0.6 and 1.7 (see Table 1). Either milliQ H_2O or ACW was added to make up suspensions having an S:L ratio of 5.0 g L^{-1}. These suspensions were equilibrated for at least 2 weeks to allow the formation of the C-S-H phases. Prior to the redox measurements, the C-S-H suspensions were centrifuged and the supernatant was transferred into polyethylene bottles and stored in a glovebox. The supernatant solutions were analysed with ICP-OES to determine the Na, K, Ca and Si concentrations. Finally, Na-dithionite was added to the solutions to obtain a final concentration of $5x10^{-3}$ M. These solutions were stored in a glovebox under inert atmosphere.

Table 1: Synthesis of alkaline reference pore waters

Solution	CaO g	Aerosil 300 g	MilliQ H_2O ml	ACW ml	pH
MQ1	0.94	1.71	500	0	~10
MQ2	2.19	0.93	500	0	12.5
ACW1	0.94	1.56	0	500	13.3
ACW2	1.63	0.92	0	500	13.3

3.2. *Fe(II)/Fe(III) samples in dilute NaCl solutions*

a. $FeCl_2$, $FeCl_3$. 1:1-buffer, 10^{-4}M each, pH 5-6 fixed with MES

c. $FeCl_2$, $FeCl_3$. 1:4-buffer, total Fe is $5 \cdot 10^{-4}$M, pH 2 fixed with HCl

3.3. *Other reference samples*

See detailed explanations from the responsible of each sample preparation.

3.4. *Natural samples*

See detailed explanations from the responsible of each sample preparation.

4. Expected outcome

It is expected that the redox potential will show a significant drift during the first couple of minutes of a measurement because of the time needed by the Pt electrode to equilibrate with the solution. The strong drift will be followed by a much slower continuous drift over an extended period of time caused by slow electrode kinetics, discussed in the introduction or arising from mixed potentials in the presence of traces of oxygen in the samples (Stumm and Morgan, 1996).

Stirring is expected to reduce significantly the electrode response time as it improves the transport of electroactive species to the electrode.

Comparison with calculated redox potentials, should give an indication for the impact of the above-mentioned kinetic processes on the measured E_h values.

5. Results and discussion

In this report, all E_h values measured during the ICE are provided. Nonetheless, only E_h measurements of the alkaline reference samples and the Fe(II)/Fe(III) containing samples will be discussed and compared with calculated E_h values. In case of the hyperalkaline reference samples, the E_h values measured by PSI will be compared with the E_h values measured by the other participants.

5.1. Summary of all results.

The results of all E_h measurements conducted by PSI during the ICE exercise are summarized in Table 2 and Table 3. Note that in these tables on the values measured after 10 minutes are given. The E_h values of the hyperalkaline solutions measured by all the participants are listed in Table 5a – 5d.

Table 2. Summary of the E_h values determined by PSI on reference samples.

Sample	pH	E_h (V)
REF 1 Fe a	8.6	-0.46
REF 1 Fe b	6.9	-0.07
REF 1 (II/III) a	5.2	0.36
REF 1 (II/III) b	2.6	0.69
REF Sus magn a	5.4	0.11
REF Sus magn b	7.7	-0.26
REF Sus magn c	7.0	-0.24
REF Sus magn d	8.3	-0.30
REF 2 Na a	5.0	0.35
REF 2 Na b	10.8	0.11
REF 2 Na c	6.3	0.20
REF 2 Na d	10.0	0.10
REF 3 HC a	5.7	0.19
REF 3 Ise a	8.0	0.14
REF 3 ISe b	5.3	-0.07
REF 4 MQ1	10.1	-0.56
REF 4 MQ2	12.5	-0.73
REF 4 MQ2 rep	12.5	-0.72
REF 4 ACW1	13.3	-0.74
REF 4 ACW1 rep	13.3	-0.77
REF 4 ACW2	13.3	-0.75
REF 4 ACW2 rep	13.3	-0.79

Table 3. Summary of the E_h values determined by PSI on natural samples.

Sample	pH	E_h (V)
NAT 1a	8.6	0.19
NAT 1a SUP	8.3	018
NAT 1b	7.1	0.15
NAT 1b SUP	6.8	0.23
NAT 2	8.0	0.25
NAT 3	9.2	0.26
NAT 3 rep	9.3	0.14
NAT 4	0.6	0.58
AA med3	7.5	-0.24
SRB med3	7.1	-0.27

5.2. Alkaline reference solutions (REF 4)

5.2.1. Electrode response time

The results of the E_h measurements in the alkaline reference samples are presented in Figure 1. Three main observations can be made: 1. E_h electrode response is generally characterized by 2 stages: a first stage showing a fast drift, followed by a second stage during which a very slow continuous drift is observed. 2. Stirring significantly reduces the time needed to reach the second stage of the electrode response. 3. E_h measurements made in the ACW-2 solution (triangles in Figure 1b) show that the electrode response strongly depends on the "history" of the electrode. Indeed, an electrode which was immersed in a redox buffer having a redox potential strongly different from the sample E_h value (E_h (buffer) = +250 mV) (half-filled triangles in Figure 1b), exhibited a much longer response time compared to an E_h electrode, which was already "adapted" to the type of samples to be measured (filled triangles). Additional observations made after the ICE, showed that this "memory" effect is stronger in samples with very dilute redox couples. Our conclusion drawn from this is that an E_h electrode should not be immersed in a redox buffer with highly concentrated redox couples prior to redox measurements on diluted samples with strongly different E_h values.

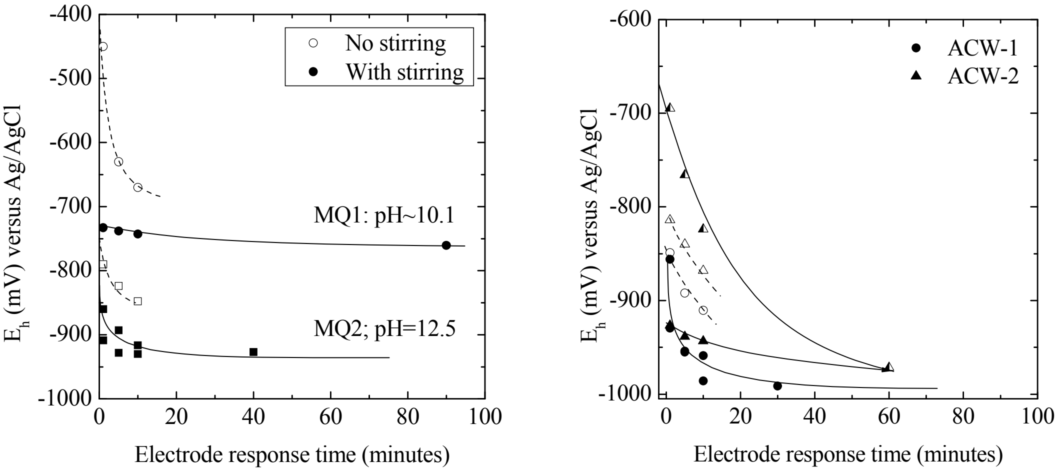


Figure 1: Response kinetics of a combined redox electrode in various alkaline cement pore waters: a. Alkali-free pore waters equilibrated with C-S-H phases with C:S ratios of 0.65(MQ1) and 1.6 (MQ2). b. Artificial cement pore waters equilibrated with C-S-H phases with C:S ratios of 0.65(ACW1) and 1.2 (ACW2).

5.2.2. Redox potential in hyperalkaline solutions

The redox potential of all the hyperalkaline reference solutions was fixed by adding Na-dithionite ($Na_2S_2O_4$) as a redox buffer. In the alkaline region the redox potential fixed by adding pure Na-dithionite varies between -0.78 V at pH = 10.0 and -1.14 V at pH = 13.3 assuming that the following reaction is valid and that SO_3^{2-} and $S_2O_4^{2-}$ are (in equilibrium conditions) in a ratio 1:1:

$$2SO_3^{2-}+2H_2O+2e^- \Leftrightarrow S_2O_4^{2-}+4OH^- \quad (E_h^0 = -1.13\ V) \qquad \text{eq. 1}$$

These E_h values are below the stability field of H_2O in this alkaline pH region. As stated above, the experimentally determined E_h is very close to the lower border of the stability field of H_2O.

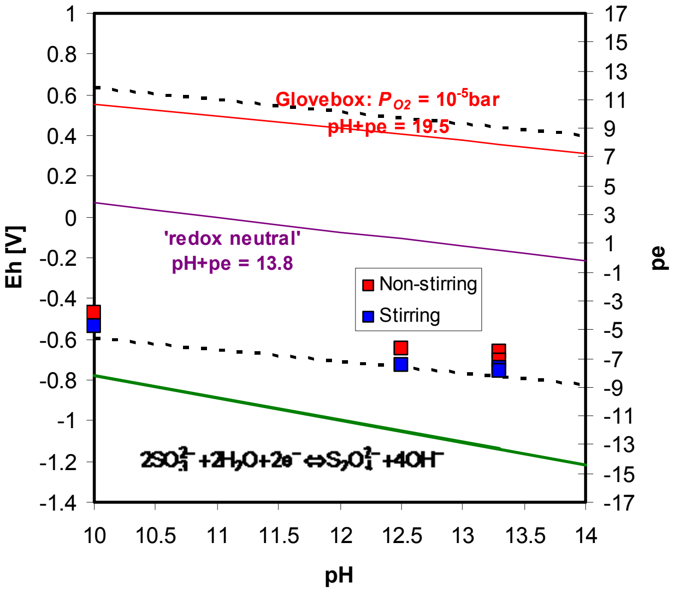


Figure 2: E_h values experimentally determined for REF 4 samples. The "thermodynamic" value is assumed to coincide with the water reduction border (also shown)

The hypothesis is raised that dithionite is oxidized by water up to a redox potential equal to the lower border of the stability field of H_2O. The H_2 generated during this process would diffuse outside the vessel. Nonetheless, kinetic effects could also prevent the reduction of water, blocking again the E_h at the limit of the water reduction. This would mean, though, that the system is not in thermodynamic equilibrium, but would not explain the measured E_h. The quantitative comparison of these experimental values with those defined by the lower limit of the H_2O stability field is provided in Table 4.

Table 4. Summary of E_H values for samples REF 4- MQ1, MQ2, ACW1 and ACW2, as determined experimentally and calculated according to the lower limit of the stability field of water.

Sample	pH	E_H PSI Experimental (V)	E_H thermodynamics Lower limit of H_2O stability field (V)
REF 4 MQ1	10.1	-0.56 ± 0.05	-0.60
REF 4 MQ2	12.5	-0.73 ± 0.05 -0.72 ± 0.05	-0.74
REF 4 ACW1	13.3	-0.74 ± 0.05 -0.77 ± 0.05	-0.78
REF 4 ACW2	13.3	-0.75 ± 0.05 -0.79 ± 0.05	-0.78

Several other participants carried out E_h measurements on the hyperalkaline solutions. A summary of the data is given in Table 5a to 5d. The measured E_h values are compared with the border of water reduction at each pH. Comparison of the E_h values measured by different participants using combined Pt electrodes shows that the reproducibility with this electrode system is very good. The recorded E_h values seem to agree reasonably well with the theoretical lower limit of the H_2O stability field. The measurements with different metal indicator electrodes (Pt, Au, GC, and pyrite) carried out by BRGM exhibited considerable variation depending on the metal used.

Table 5a: Summary of measured E_h values for MQ1 (pH = 12.5; Theoretical E_h value = -0.59 V.

Partner	Electrode system	Measuring time (Minutes)	Measured E_h (V)
BRGM	Pt disk shaped	40	-0.40
	AU disk shaped		-0.55
	GC disk shaped		-0.47
	Pyrite 1		-042
	Pyrite 2		-0.51
Ulough	Pt-wire	90	-0.597
Amphos	Pt comb.		-
IPL	Pt comb.		-
PSI	Pt comb.	10 (no stirring)	-0.47
		10 (stirring)	-0.54
		90 (stirring)	-0.56

Table 5b: Summary of measured E_h values for MQ2 (pH = 10.1; Theoretical E_h value = -0.74 V.

Partner	Electrode system	Measuring time (Minutes)	Measured E_h (V)
BRGM	Pt disk shaped	71	-0.43
	AU disk shaped		-0.68
	GC disk shaped		-0.57
	Pyrite 1		-045
	Pyrite 2		-0.63
Ulough	Pt-wire	90	-0.663
Amphos	Pt comb.		-
IPL	Pt comb.		-
PSI	Pt comb.	10 (no stirring)	-0.64
		10 (stirring)	-0.72
		90 (stirring)	-0.72

Table 5c: Summary of measured E_h values for ACW1 (pH = 13.3; Theoretical E_h value = -0.79 V.

Partner	Electrode system	Measuring time (Minutes)	Measured E_h (V)
BRGM	Pt disk shaped	25	-0.35
	AU disk shaped		-0.71
	GC disk shaped		-0.69
	Pyrite 1		-057
	Pyrite 2		-0.72
Ulough	Pt-wire	90 (stirring)	-0.614
Amphos	Pt comb.	25 (stirring)	-0.76
IPL	Pt comb.	30 (stirring)	-0.71
PSI	Pt comb.	10 (no stirring)	-0.66
		10 (stirring)	-0.74
		90 (stirring)	-0.77

Table 5d: Summary of measured E_h values for ACW2 (pH = 13.3; Theoretical E_h value = -0.79 V.

Partner	Electrode system	Measuring time (Minutes)	Measured E_h (V)
BRGM	Pt disk shaped	71	-0.46
	AU disk shaped		-0.74
	GC disk shaped		-0.67
	Pyrite 1		-04
	Pyrite 2		-0.7
Ulough	Pt-wire	803	-0.606
Amphos	Pt comb.	45 (stirring)	-0.77
IPL	Pt comb.	30 (stirring)	-0.77
PSI	Pt comb.	10 (no stirring)	-0.64
		10 (stirring)	-0.72
		90 (stirring)	-0.72

5.3. Fe(II) / FE(III) containing solutions (REF I (II/III) a and REF 1 (II/III) c)

The comparison of experimental data with thermodynamic calculations was limited (in the case of PSI) to Fe samples in dilute NaCl systems, i.e. REF 1 (II/III) a and REF 1 (II/III) c. Description of the samples given by the organizers, as well as additional observations collected during the ICE are summarized below:

5.3.1. Observations during the exercise:

Sample a
Yellow-orange colored solution, with some precipitate of similar color.
pH = 5.2
$E_H = 0.36$ V

Sample c
Yellow-orange colored solution. Slightly turbid solution, but no clear precipitate observed, as in the previous case.
pH = 2.6
$E_H = 0.69$ V

In addition to this information, the redox speciation of Fe in these samples was determined by one of the participant groups (Regina Kirsch, David Fellhauer). These data are summarized in Table 6.

Table 6. Information on the Fe content and speciation (Kirsch, personal communication).

Sample	Dilution for measurements	Fe_{tot} [M]	Fe(II) [M]	Fe(III) [M]	% Fe(II) / Fe_{tot}
Fe(II/III) a	1:100	9.038E-05	9.395E-05	-3.576E-06	104.0%
Fe(II/III) a repetition	1:10	9.776E-05	9.552E-05	2.241E-06	97.7%
Fe(II/III) c	1:10	1.560E-04	1.002E-04	5.586E-05	64.2%

All concentration values are given for the undiluted solutions

5.3.2. Thermodynamic database used in the calculations

A TDB for Fe aqueous species was compiled for the system Fe(II)-Fe(III)-H_2O-Cl. Reactions, corresponding equilibrium constants and sources considered for the data selection are provided in Table 7.

Table 7. Thermodynamic data selected for Fe(II) and Fe(III) aqueous species involved in this exercise.

Reaction	$\log_{10}K°$	Reference
$Fe^{2+} + H^+ = Fe^{3+} + 0.5H_2(g)$	-13.051 ± 0.160	Calculated internally from $\Delta_rG°_m$. $E°(Fe^{3+}/Fe^{2+})$ determined from [2000TAG/DIA], [1972WHI/LAN], [1953MAG/HUI], [1951CON/MCV], [1929POP/KUN], [1937SCH/SHE], [1934BRA/HER]
$Fe^{2+} + H_2O = FeOH^+ + H^+$	-9.100 ± 0.400	Calculated from $\log_{10}{}^*\beta°_{s,1}$ and $\log_{10}{}^*\beta°_{s,0}$ of magnetite determined from solubility data in [1970SWE/BAE] and [1980TRE/LEB]
$Fe^{2+} + 2H_2O = Fe(OH)_{2(aq)} + 2H^+$	-21.2 ± 1.1	Calculated from $\log_{10}{}^*\beta°_{s,2}$ and $\log_{10}{}^*\beta°_{s,0}$ of magnetite determined from solubility data in [1970SWE/BAE] and [1980TRE/LEB]
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	-2.150 ± 0.070	Calculated applying SIT to data provided in [2007SVE], [2000BYR/LUO], [1986KHO/BRO], [1979ZOT/KOT], [1977SAP/PAT] and [1955MIL/VOS]
$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	-4.8 ± 0.4	Weighed SIT from data provided in [1990SAL/VAS], [1986KHO/BRO] and [1977SAP/PAT]
$2Fe^{3+} + 2H_2O = Fe_2(OH)_2^{4+} + 2H^+$	-2.820 ± 0.110	Weighed SIT from data provided in [2007STE], [1990SAL/VAS], [1986KHO/BRO], [1977SAP/PAT], [1973VER/RAN], [1957MIL], [1955MIL/VOS] and [1953HED]
$Fe^{3+} + 3H_2O = Fe(OH)_{3(aq)} + 3H^+$	≤ -14	Determined from a ferrihydrite solubility study in [2007STE]
$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	-21.5 ± 0.5	Determined from a ferrihydrite solubility study in [2007STE]
$Fe^{3+} + Cl^- = FeCl^{2+}$	1.520 ± 0.100	SIT from data provided in [1989BRU/PET], [1981BYR/KES], [1976ASH], among others
$Fe^{3+} + 2Cl^- = FeCl_2^+$	2.220 ± 0.224	SIT from data provided in [1979STR/PAT], [1976SCH/DOD], [1969MOR/WIL] [among others], in combination with $\log_{10}K°_1$
$Fe^{3+} + 3Cl^- = FeCl_{3(aq)}$	1.020 ± 0.300	Average of the results in [2006LIU/ETS], [1960MAR] and [1942RAB/STO], in combination with $\log_{10}K°_1$ and $\log_{10}K°_2$

5.3.3. Comparison exercise

Experimental E_h values determined by PSI and speciation information available on the Fe(II)/Fe(III) couple were compared with thermodynamic calculations conducted with the thermodynamic database compiled in section 1.1.

The predominance diagram in Figure 3 shows samples “REF 1 (II/III) a” and “REF 1 (II/III) c” (represented as experimental E_H and pH measurements) in the context of Fe(II)/Fe(III) aqueous speciation. Solid blue lines in the diagram represent a 50:50 ratio of the aqueous species at each side of the line. According to Figure 3, both samples should be enriched in Fe(II), although in the case of sample REF 1 (II/III) c the ratio Fe(II):Fe(III) should be closer to 1. Both statements are confirmed by the redox speciation provided in Table 6.

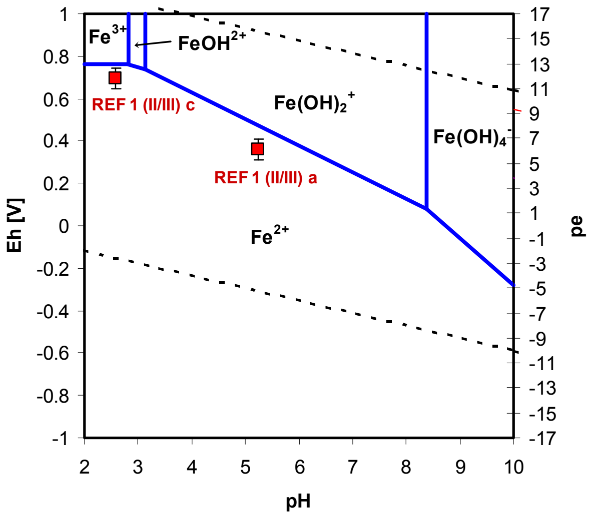
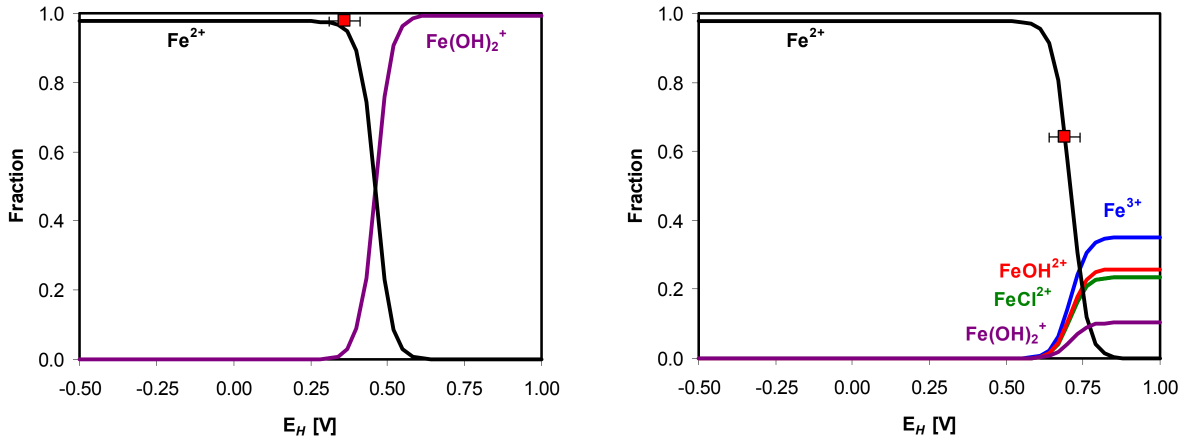


Figure 3. Predominance diagram of aqueous Fe species for $-1V \leq E_H \leq +1V$ and $2 \leq pH \leq 10$. Red squares correspond to experimental E_H and pH values measured for samples REF 1 (II/III) a and REF 1 (II/III) c.

In order to properly calculate the thermodynamic E_H of both samples, one should know beforehand the plausible species involved in the redox equilibrium. For this purpose, fraction diagrams within $-0.50V \leq E_H \leq 1.0V$, fixed pH (experimental PSI) and fixed $[Cl^-]$ (available for each sample) were calculated for both samples (Figures 4 a and b). Experimental E_H values in combination with Fe redox speciation are appended to the figure (red squares).



a **b**

Figure 4. Fraction diagram of Fe for -0.5V ≤ E_H ≤ + 1.0V, and pH = 5.2 **(a)** or pH = 2.6 **(b)**. Red square corresponding to experimental E_H and Fe(II)-Fe(III) ratios.

5.3.3.1. Calculation of E_H^{therm}(REF 1 (II/III) a)

Only two species (Fe^{2+} and $Fe(OH)_2^+$) are needed to calculate the E_H^{therm} for sample REF 1 (II/III) a (see Figure 4a). The redox equilibrium reaction considered and the corresponding logK value are provided in rx. 1 and eq. 2.

$$Fe^{2+} + 2H_2O \Leftrightarrow Fe(OH)_2^+ + 2H^+ + 1e^- \qquad \text{rx. 1}$$

$$\log K^0_{Fe^{2+}-Fe(OH)_2^+} = \log\left([Fe(OH)_2^+]\cdot\gamma_{Fe(OH)_2^+}\right) - \log\left([Fe^{2+}]\cdot\gamma_{Fe^{2+}}\right) - 2pH + 2\log\gamma_{H^+} - pe \qquad \text{eq. 2}$$

The re-organization of eq. 2 allows the calculation of pe (equation eq. 3).

$$pe = \log\left([Fe(III)]_{tot}\cdot\gamma_{Fe(OH)_2^+}\right) - \log\left([Fe(II)]_{tot}\cdot\gamma_{Fe^{2+}}\right) - \log K^0_{Fe^{2+}+Fe(OH)_2^+} - 2pH + 2\log\gamma_{H^+} \qquad \text{eq. 3}$$

In the case of sample REF 1 (II/III) a, the calculation of pe is direct because the simplifications below can be done straight forward:

$[Fe^{2+}] = [Fe(II)]_{tot}$
$[Fe(OH)_2^{+}] = [Fe(III)]_{tot}$

Resulting in the pe (and therefore E_H^{therm}) provided below:

$pe = 4.2 \Rightarrow E_H^{therm} = 0.25$ V

The calculated E_H^{therm} does not compare very well with E_H^{exp} (0.36 ± 0.05 V), probably because the ratio Fe(II)-Fe(III) in the sample is very high, therefore experimentally hindering the appropriate quantification of the redox speciation. As shown above, this is a mandatory input in the process of E_H^{therm} calculation.

5.3.3.2. Calculation of E_H^{therm}(REF 1 (II/III) c)

As shown in Figure 4b, the number of species involved in the redox equilibrium in sample REF 1 (II/III) c is much higher, and therefore a slightly different approach has been considered for the calculation of the E_H^{therm}. In this case, the reaction chosen to calculate pe and the corresponding logK are shown in rx. 2 and eq. 4:

$$Fe^{2+} \Leftrightarrow Fe^{3+} + 1e^{-} \qquad \text{rx. 2}$$

$$\log K^{\circ}_{Fe2+-Fe3+} = \log([Fe^{3+}]\cdot\gamma_{Fe3+}) - \log([Fe^{2+}]\cdot\gamma_{Fe2+}) - pe \qquad \text{eq. 4}$$

As in the previous case, $[Fe^{2+}] = [Fe(II)]_{tot}$. Nonetheless, for this sample $[Fe^{3+}] \neq [Fe(III)]_{tot}$ and further hydrolysis products and chloride species have to be taken into account for Fe(III). Based on Figure 4b, $[Fe(III)]_{tot}$ can be defined as:

$$[Fe(III)]_{tot} = [Fe^{3+}] + [FeOH^{2+}] + [FeCl^{2+}] + [Fe(OH)_2^{+}],$$

which combined with equation eq. 4 leads to eq. 5 for the determination of pe.

$$\mathrm{pe}=\log\left([\mathrm{Fe(III)}]_{\mathrm{tot}}\cdot\gamma_{\mathrm{Fe^{3+}}}\right)-\log\left([\mathrm{Fe(II)}]_{\mathrm{tot}}\cdot\gamma_{\mathrm{Fe^{2+}}}\right)-\ldots \qquad \text{eq. 5}$$

$$\ldots-\log K^{0}_{\mathrm{Fe^{2+}-Fe^{3+}}}-\log\left(1+\Sigma\beta^{0}_{n,H,L}\cdot[\mathrm{Cl^{-}}]^{n}\cdot[\mathrm{H^{+}}]^{-n}\right)$$

allowing the calculation of the pe (and E_H^{therm}):

pe = 11.8 ⇒ $E_H^{\mathrm{therm}} = 0.70$ V

In this case, the agreement of the calculated E_H^{therm} with E_H^{exp} (0.69 ± 0.05 V) is significantly better. This is very likely due to the higher concentration of Fe and the more proportional ratio of Fe(II)-Fe(III), which make the experimental redox speciation of Fe more robust.

6. Conclusions

The following conclusions can be drawn from this exercise:

- Combined redox electrodes appear to be reliable tools for the study of reference (buffered) samples.
- Larger degree of uncertainty is observed with natural samples where concentrations of the buffering redox couple(s) are lower.
- Stirring improves significantly the response time and reliability of the measurements.
- “Memory effect” can be significant after measurement of strongly buffered systems.

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ReCosy, Intercomparison Exercise

Within Workpackage 2 “Development of redox determination methods”

Short summary description

UKOE(AG), KIT INE(1), TUG(14):

Determination of redox species of iodine and iron with CE-ICP-MS

Bernhard Kuczewski, Markus Lagos, Christian M. Marquardt, Edit Marosits, Corinna Dully

Background and Objectives

Beside the measurement of the redox potential by electrochemical and optical sensors the determination of the occurring species like Fe(II) and Fe(III) or iodine and iodate gives additional data validating the measured values. By applying these particular speciation methods it has to be ensured that they are not influencing the redox speciation during the separation process. Capillary electrophoresis (CE) combined with ICP-MS is a useful method that can be optimised to prevent the separated oxidation states from redox processes by the formation of strong complexes. The system for iodine and iodate determination was developed and tested within the scope of the RECOSY project at TUG, the separation of the iron species was taken from the literature.

The results of the CE-ICP-MS measurement support the interpretation of results obtained by electrochemical and spectroscopic methods. From the determined ratios of Fe(II) and Fe(III) the redox potential of the solutions can be calculated and compared with measured redox potentials of other groups participate in the ICE.

Experimental method and approach

The separation of oxidation states by CE-ICP-MS utilises the different charge to ionic radius ratios between the distinct species (for example iodine and iodate). The sample is injected into an electrolyte filled fused silica capillary (50µm ID) by pressure. After that a high voltage (30KV) is applied to separate the ions. As a result of their differing mobilities in the electric field they are fixed in well separated zones. At the end of the capillary these zones are sucked consecutively into the nebuliser of the ICP-MS. The elements are finally detected and determined quantitatively by the mass spectrometer in the ICP-MS.

Iodate and iodine can be separated directly and the change of the redox speciation of iodine during the separation is negligible. The buffer used for the separation is acetic acid. If the ions can not be separated directly like in the case of Fe(II) and Fe(III), the species can also be segregated as strong complexes. Here, Fe(III) is complexed by EDTA and Fe(II) by 1,10-phenantroline. To form the complexes the sample is mixed with small amounts of a concentrated complexing agent solution. The so formed strong complexes prevent the species from further oxidation or reduction. As an appropriate electrolyte a borate buffer (pH 9) is applied.

Solutions to be measured

The samples of the ICE program that can be investigated are restricted to those that have similar pH and ionic strength as the electrolytic separation system. Strong alkaline solutions are not suitable.

There are eleven solutions that should be measured, namely:

a. REF 1 Fe a,
b. REF 1 Fe b,
c. REF (II/III) a,
d. REF (II/III) c,
e. REF HC,
f. REF ISe a,
g. REF ISe b,
h. NAT 1a,
i. NAT 1b,
j. NAT 2 and
k. NAT 3.

Expected outcome

We expected that we are able to determine the amount of the occurring species of iron and iodine in different sample solutions. The Eh value of the samples can be calculated from the measured concentration ratios of Fe(II)/Fe(III) and I(-I)/I(V) by using an appropriate thermodynamic model .

Outcome of the study

The measurement of the samples had to postpone after the ICE period due to unforeseen technical problems with the CE-ICP-MS system.

RECOSY INTERCOMPARISON EXERCISE

WORKPACKAGE 2

A report prepared by :

Sneh L. Jain and Mónica Felipe-Sotelo

17th December 2009

Loughborough University

ReCosy Intercomparison Exercise Workpackage 2

Study within the work package “Development of Redox determination methods”

1. Background and objectives

Previous experience within the Radiochemistry group at Loughborough University has shown drifting of the Eh value at various measurement times as well as poor reproducibility (measurements of Eh are made under inert nitrogen atmosphere, with both commercial and in-house Pt-wire electrodes). Consequently, it was decided to use one fixed time for comparison purposes within individual studies. Although this is comparable within our laboratory, it is not necessarily comparable with systems measured by other groups. It is hoped that this exercise will allow the development of a protocol which will mean the comparison of data with other groups is more viable.

The objectives are as follows:

(i) Assessment of drift for different stabilisation times:

(a) Stabilisation time is monitored with reference electrode left in the solution.

(b) Working electrode alone is left in to stabilise with solution.

(ii) Comparison of the effect of the nature of the sample solution for example hyperalkaline solution representative of the environment of the near field of a intermediate level waste (ILW) repository versus a humic acid containing solution, which is representative of far field conditions.

(iii) Comparison of the results with other groups running the same samples using different experimental conditions (e.g. sample homogenisation or type of working electrodes).

2.- Experimental method and approach

The experimental setting used for the measurement of samples is shown in **Figure 1**. The redox potentials were measured using Pt-wire working electrodes versus a commercial Metrohm Ag/ $AgCl_2$ electrode. Solutions were measured under stagnant conditions. The working electrode was pre-treated by washing in dilute nitric acid and stored in deionised water. All measurements were conducted at ambient temperature in an Ar glovebox with oxygen contamination of solutions and equipment avoided by standard lab procedures for work under anaerobic conditions.

Samples were observed at various time intervals by continuous measurement of the Eh value. Initial expectations were around 1 hour, but were measured up to 24 hours. Electrodes were washed thoroughly between samples.

Figure 1.- Experimental setting

3.- Solutions measured

The radiochemistry group at Loughborough University focuses its research interest on the study of the behaviour and transport or radionuclides in the near field of intermediate level waste (ILW) repository, as well as in the far field. Accordingly, several sets of samples have been chosen and measured during the intercomparison exercise, which are representative of both types of conditions:

a.- Samples would be representative of the dominant conditions in a ILW repository.

a.1.- Systems under hyperalkaline conditions (prepared by Dr J. Tits at PSI):

- Ref 4 MQ1 ([Ca]= 10^{-4} mol dm^{-3}; [Si] = 10^{-2} mol dm^{-3}; [Na] = 0 mol dm^{-3}; [K] = 0 mol dm^{-3}).

- Ref 4 MQ2 ([Ca]= 10^{-2} mol dm^{-3}; [Si] = 10^{-5} mol dm^{-3}; [Na] = 0 mol dm^{-3}; [K] = 0 mol dm^{-3}).

- Ref 4 ACW1 ([Ca]= 10^{-4} mol dm^{-3}; [Si] = 10^{-2} mol dm^{-3}; [Na] = 0.11 mol dm^{-3}; [K] = 0.18 mol dm^{-3}).

- Ref 4 ACW2 ([Ca]= 10^{-2} mol dm^{-3}; [Si] = 10^{-5} mol dm^{-3}; [Na] = 0.11 mol dm^{-3}; [K] = 0.18 mol dm^{-3}).

a.2.- Fe systems in salt brine:

- Ref2 Ca b – Redox control: $FeCl_2$/ $FeCl_3$; ([$CaCl_2$]= 2 mol dm^{-3}; [$FeCl_2$] = 10^{-4} mol dm^{-3}; [$FeCl_3$] = 10^{-4} mol dm^{-3}) pH = 12 (fixed with $Ca(OH)_{2\,(s)}$).

b.- Samples representative of the conditions in the far field of a repository:

b.1.- Ground water with humic substances (Gorleben):

- NAT 1a – Gorleben soft humic rich groundwater, dilute, very much humics, conditioned in a fridge since 03.07.1991.

- NAT 1b – Gorleben, deep channel brines, conditioned in a fridge since 02.12.1993.

b.2.- Clay-rock system (COX):

- NAT 2 – sample with COX (clay-rock system) characteristics.

b.3.- Granitic groundwater (Grimsel):

- NAT 3 – Grimsel groundwater, granitic, very low content of dissolved species.

c.- High salinity/brine conditions:

- NAT 4 – Magnesium rich high salinity brine.

4.- Expected outcome

The expected outcome of the intercomparison exercise is to achieve the agreement of a suitable protocol for the measurement of Eh that provides comparable inter- and intra-laboratory results for samples of different origin.

5.- Outcome of the study

5.1.- *Experimental results*

5.1.1.- Systems under hyperalkaline conditions

Figure 2 shows the continuous measurement of the Eh value (against the Ag/AgCl reference electrode) of the sample Ref4 MQ1. After 18 minutes, the reference electrode was removed from the sample, while the working electrode was kept in contact with it. After 80 min the reference electrode was introduced once more in the sample. It can be observed that the measurements achieved steady state after approximately 2 hours. Similar tendency was observed for the sample Ref4 MQ2, which reached steady state after ca. 90 min (**Figure 3**).

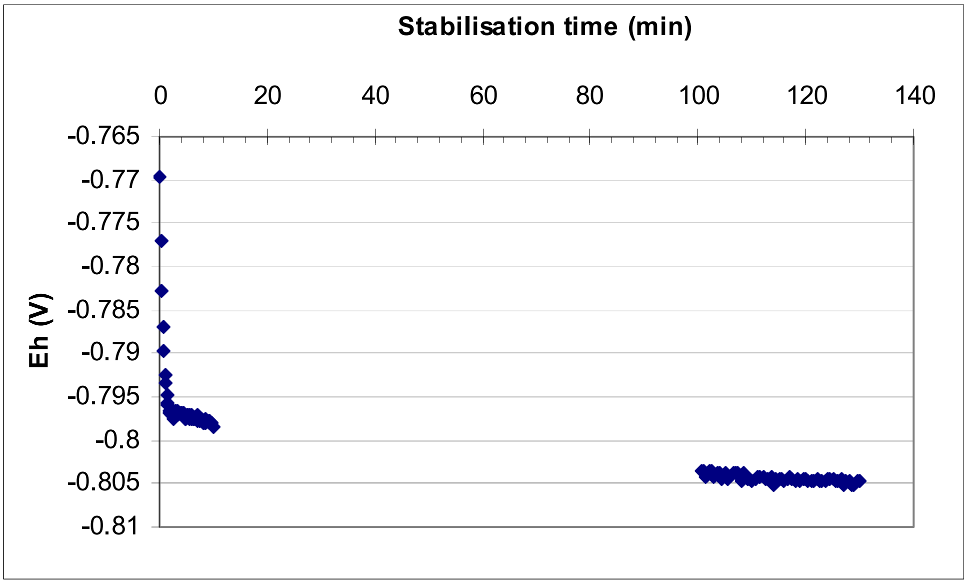

Figure 2.- Continuous Eh measurement of the sample Ref 4 MQ1
(Eh values against the Ag/AgCl electrode)

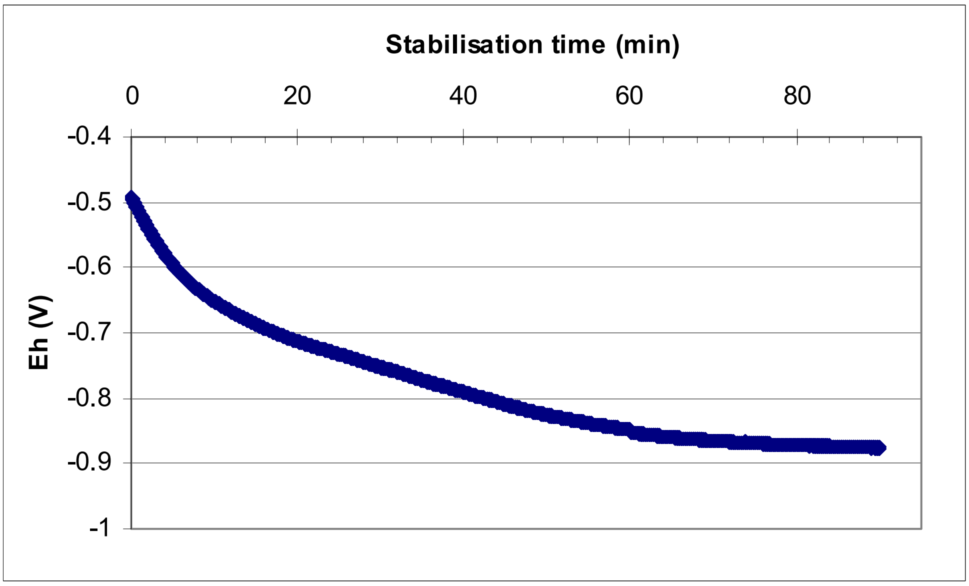

Figure 3.- Continuous Eh measurement of the sample Ref 4 MQ2
(Eh values against the Ag/AgCl electrode)

The samples labelled as ACW were prepared in artificial cement pore water, and consequently had a higher pH and ionic strength than samples MQ1 and 2, prepared in deionised water. Sample ACW1 (**Figure 4**) was measured overnight, with both electrodes, working and reference submerged in the sample. It was observed that the Eh measurement achieved steady state after 3 hours, and did not suffer significant changes for the following 13 hours. The ionic strength of this sample could be the cause of the longer stabilisation time required for this sample, when compared with MQ1 and 2.

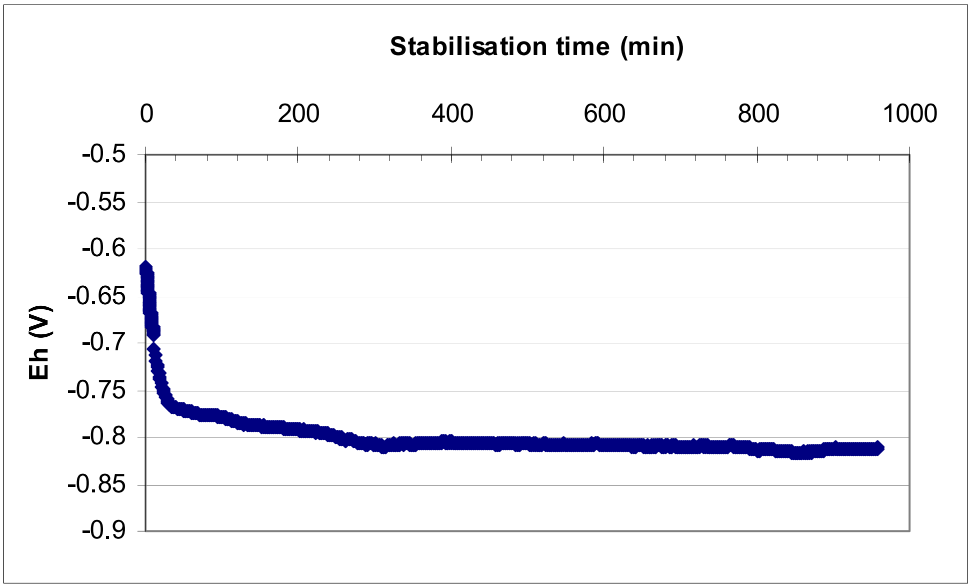

Figure 4.- Continuous Eh measurement of the sample Ref 4 ACW1
(Eh values against the Ag/AgCl electrode)

In the case of ACW2, the working electrode was kept in the sample overnight, whilst the reference electrode was kept outside the sample (**Figure 5**).

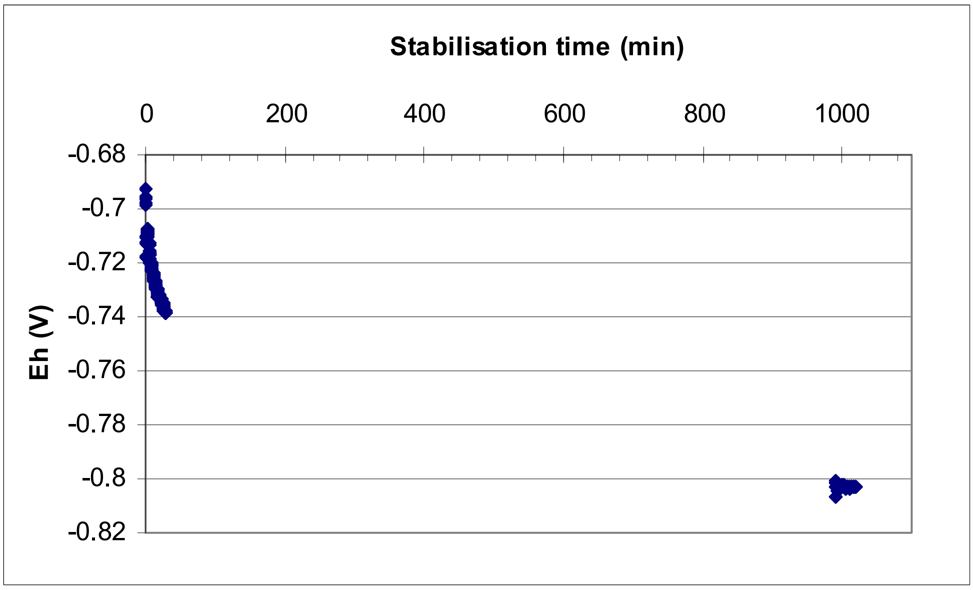

Figure 5.- Continuous Eh measurement of the sample Ref 4 ACW2 (Eh values against the Ag/AgCl electrode)

5.1.2.- Fe systems in salt brine

Figure 6 shows that the measurement of the sample Ref2 Ca b required about 90 min of stabilisation time, before achieving a constant Eh value.

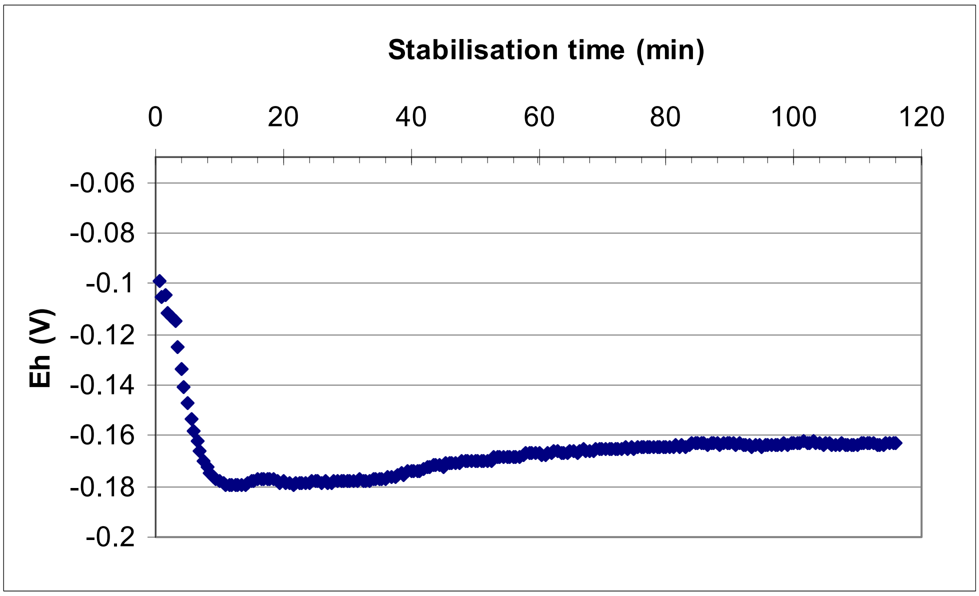

Figure 6.- Continuous Eh measurement of the sample Ref 2 Ca b (Eh values against the Ag/AgCl electrode)

5.1.3.- Ground water with humic substances (Gorleben)

Figure 7 illustrates the results obtained for Nat1 a, the sample with the highest content in organic matter. It can be observed that the behaviour is rather erratic; after 20 min of continuous measurement the Eh reached a plateau and kept stable for 80 min (see insert in **Figure 7**), and after 100 min of stabilisation the signal began to decrease steadily, reaching a new plateau after 18 hours. This behaviour suggests that the organic content of the sample changes the properties of the surface of the electrode during the stabilisation. To confirm this hypothesis, careful examinations of the electrode surface, as well analysis of the total organic content in the sample before and after the measurement, would be required.

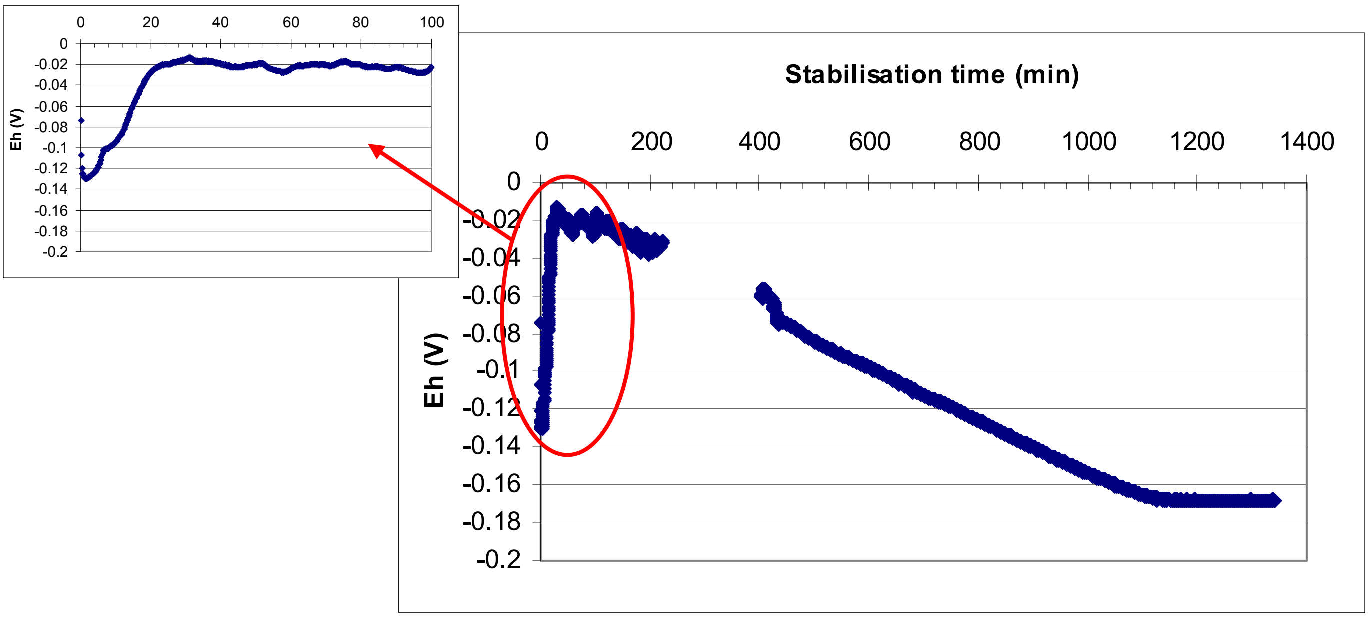

Figure 7.- Continuous Eh measurement of the sample Nat1 a
(Eh values against the Ag/AgCl electrode)

Sample Nat 1b has a lower concentration of organic matter and, as it can be observed in **Figure 8**, did not behave in the same erratic way as sample Nat 1a. This sample reached a stable value of Eh after 3 hours of continuous measurement, and the same value was registered after 20 hours (note that whereas the working electrode was kept in the sample during the whole duration of the experiment, the reference electrode was removed from the solution overnight).

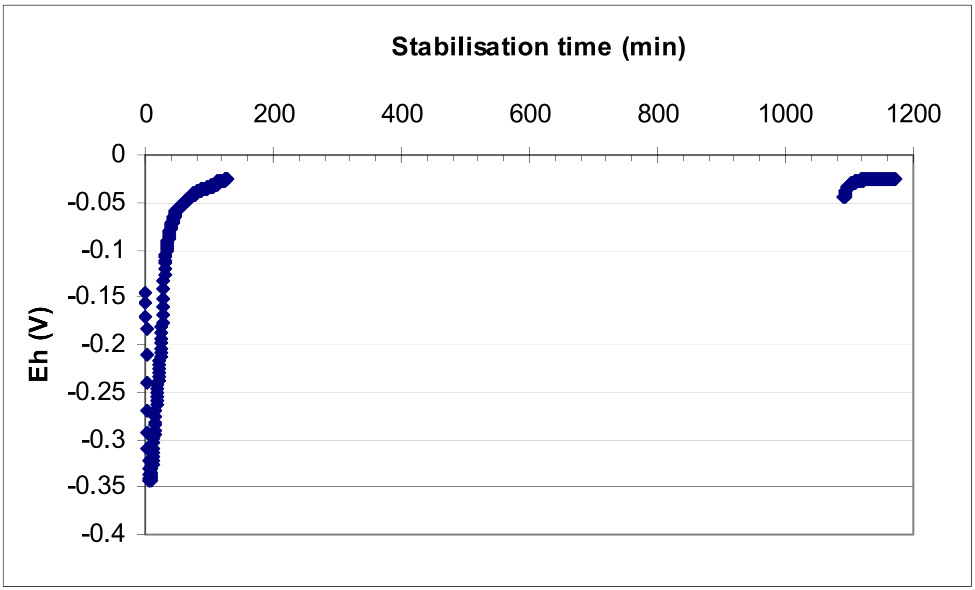

Figure 8.- Continuous Eh measurement of the sample Nat1 b
(Eh values against the Ag/AgCl electrode)

5.1.4.- Clay-rock system (COX)

The results obtained for the sample Nat2 are shown in **Figure 9**. The Eh measurement required 13 hours to achieve an stable value. After a fast decrease of the Eh value after the 1st hour of measurements, the Eh value kept on decreasing steadily, and finally reached a plateau at -120 mV (against Ag/AgCl electrode) after 13 hours.

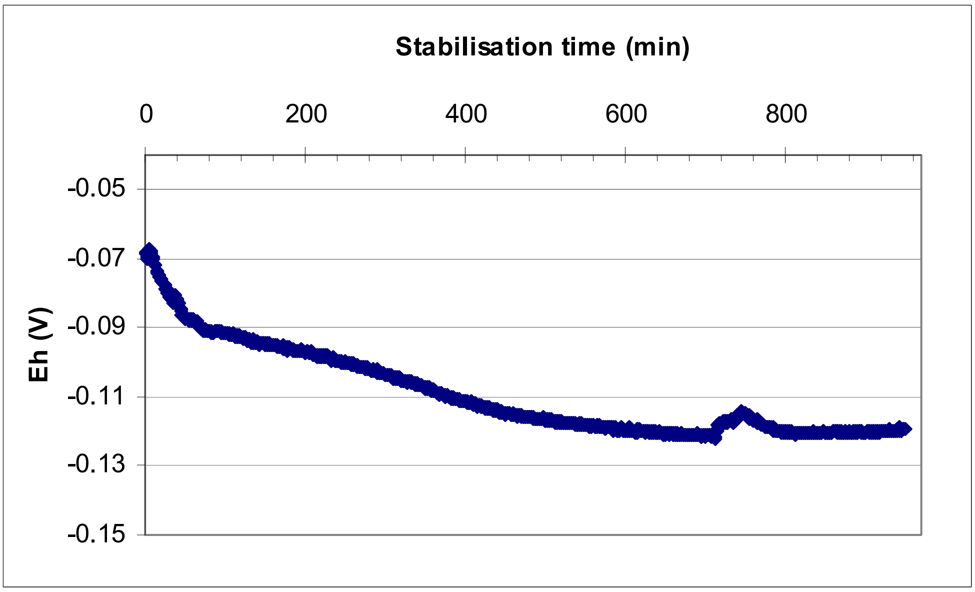

Figure 9.- Continuous Eh measurement of the sample Nat2
(Eh values against the Ag/AgCl electrode)

5.1.5.- Granitic groundwater (Grimsel)

Sample Nat3 reached a stable value of Eh after 2 hours of stabilisation (**Figure 10**) with both working electrode and Ag/AgCl reference electrodes in the sample during the whole experiment.

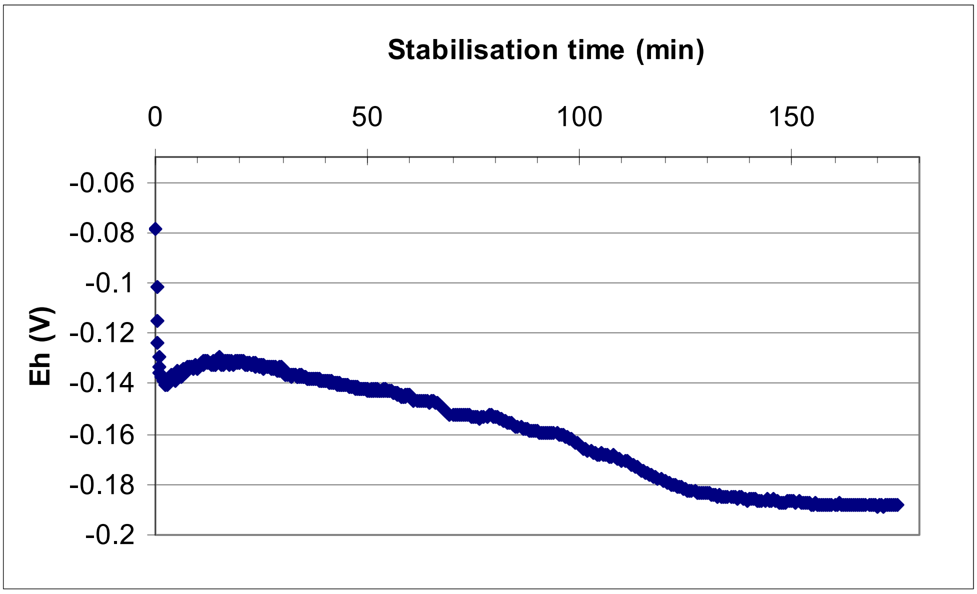

Figure 10.- Continuous Eh measurement of the sample Nat3
(Eh values against the Ag/AgCl electrode)

5.1.6.- High salinity / brine conditions

As it can be observed in **Figure 11**, the Eh measurement of the sample Nat 4 quickly achieved a stable value in 30 min.

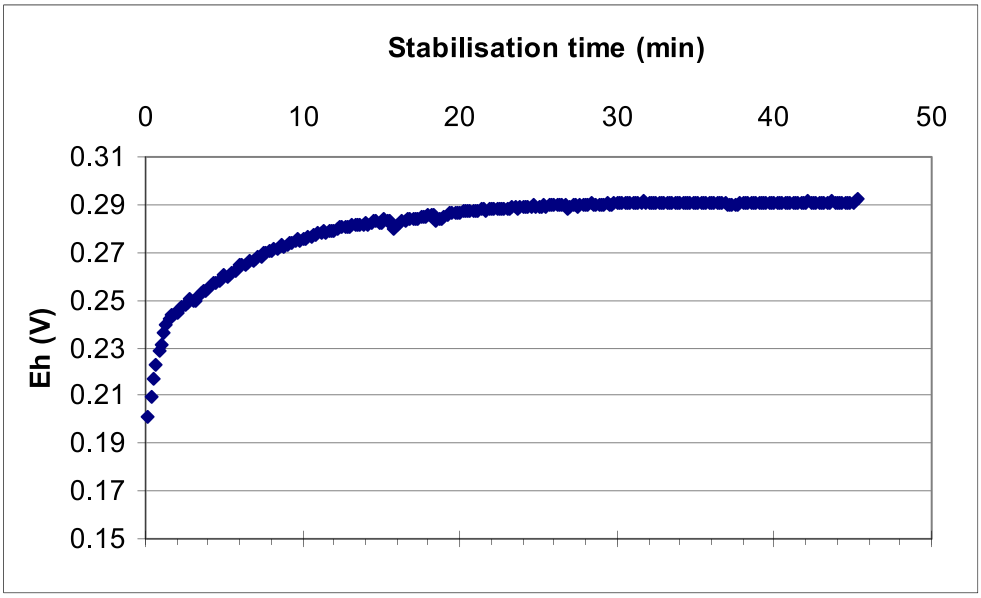

Figure 11.- Continuous Eh measurement of the sample Nat4
(Eh values against the Ag/AgCl electrode)

5.1.7.- Summary of results

Table 1 shows the experimental results obtained for all samples at the steady state. Note that, despite the measurements were performed against a Ag/AgCl electrode, the Eh values have been corrected, considering the hydrogen electrode as reference. **Table 1** also includes the time required for the stabilisation of the Eh measurement.

Table 1.- Measured Eh values using a Pt-wire electrode with respect to hydrogen reference electrode

	Sample	**Eh value (mV)**	**Stabilisation time (min)**
Hyperalkaline solutions	REF 4 MQ1	-597	110
	REF 4 MQ2	-663	76
	REF 4 ACW1	-614	320
	REF 4 ACW2	-606	1000*
Humic samples	NAT 1a	+185	90
	NAT 1b	+171	1150*
Clay-rock system (COX)	NAT 2	+87	950
Granitic groundwater	NAT 3	+18	176
High salinity / brine conditions	NAT 4	+487	13
Fe systems in salt brine	REF2 Ca b	+34	42

* These samples were left to stabilise overnight with the reference electrode outside the sample. Although the Eh values were registered at the times shown, the stabilisation of the signal may have required shorter times than indicated

5.1.- *Conclusions*

Overall, samples with higher ionic strength, for example REF 4 ACW1, required relatively long stabilisation times. However, samples containing high concentrations of organic matter such as NAT 1a required even longer stabilisation times (24 hours). In the case of samples which have humic acid content showed erratic behaviour of the Eh value as a function of time. It is suspected that the electrode surface is undergoing a chemical change (co-ordination of organic species) rendering a modified electrode surface. This phenomenon requires further investigation.

It must be noted that during these experiments the stability of the Eh measurements was the main parameter taken into account. However, the stability of the signal alone does not ensure accurate results, as changes in the electrodes and solutions may occur.

ReCosy ICE Report

ReCosy Intercomparison Exercise: Statistical analysis

16 – 20 November 2009, Karlsruhe

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Loughborough University

1-. Introduction and Objectives

The objective of this report is to provide a simple statistical analysis of the results of the ReCosy Intercomparison Exercise. It has not been intended to provide the real value of Eh, since that would require a deeper knowledge of the reasons that are causing the large variation observed in most of samples. It was not the intention either, to judge or qualify the performance of any of the participant groups, therefore any scoring (usual in proficiency test) has been also avoided.

The data obtained during the ReCosy Intercomparison Exercise have been presented graphically and the basic statistic parameters, average standard deviation (SD), relative standard deviation (RSD) and median have been calculated (see definitions in section 2). Box-whiskers plots and frequency histogram have been also plotted in order to provide a better view of the distribution/dispersion of data, as well as detection of outliers.

Regarding the data considered in this study, on any occasion that the Eh measurement was left to equilibrate and a time resolved signal was provided, the last Eh value of the time series was considered, unless otherwise stated by the participant group. All the replicates measurements were included in the analysis, regardless the technique, procedure or participant.

2. Definitions

- <u>Average</u>: This refers to the arithmetic mean of the data series (sum of the replicate value divided by the number of observations).

- <u>Standard deviation</u>: The standard deviation is defined as the square root of the variance (sum of square values of the deviation of the experimental value against the average, divided by the degrees of freedom).

- <u>Relative standard deviation</u>: This parameter is an indicator of the reproducibility of the analysis. It is calculated by dividing the standard deviation by the mean of the same set of data. It is often expressed as percentage.

-<u>Median</u>: the median corresponds to the central value of a series of data. In the case of an even number of data, the median is calculated as the average of the two central values. Usually the median is not as good as the average to estimate the real value of a measurement, however, the median is less sensitive to scattering of the experimental results. When the results are affected by a big dispersion, the median could be a better estimation of the real vale than the average.

- <u>Box-plot</u>: in the box-and-whiskers plots, the boxes have lines at the lower quartile, median and upper quartile vales. The whiskers are line extending from each of the boxes to show the extent of the rest of the data. The outliers are data with values beyond the ends of the whiskers.

- <u>Frequency histograms</u>: to build up the histograms, the experimental range of results has been divided in ten equally spaced intervals, and the number of element s or result in each interval has been counted and plotted.

3. Samples

3.1 Dilute Fe systems (REF 1)

3.1.1 REF 1 Fe a

Table 1 shows the results of the 21 replicates performed for sample REF 1 Fe a. Results spread in a wide range of Eh values from -457 to +457 mV. Figure 1 and the frequency histogram in Figure 3 show that the 3 replicates from ITU and the first measurement from BRGM with the Pt electrode constitute a separate group of results with positive Eh values, whereas all the other measurements give negative values that gather around -250 mV.

Table 1.- Summary of the results obtained for sample REF 1 Fe a

Institution	Method/Replicate	Eh (mV)
Amphos	1	-295
	Cleaning (Toothpaste) 1	-395
	2	-344
	Cleaning (Toothpaste) 2	-320
FZD	Suspension	-349
	Filtrate	-73.9
	Supernatant	-230.8
ITU	Comb Pt Stirred	402
	Comb Pt Static	431
	Comb Au Stirred	306
MSU-INE	Prot 1	-264
	Prot 2	-216
	Prot 3	-356
	Prot 4	-259
PSI		-456.6
BRGM	Pt	52.69
	Au	-107.04
	GC	-123.32
	Pt disc	-143.68
CNRS	Amperometric: Pt UME glass	-271.6
	Potentiometric: Pt RDE	-192.3
Statistics	**Average**	-153
	SD	252
	RSD (%)	165
	Median	-231

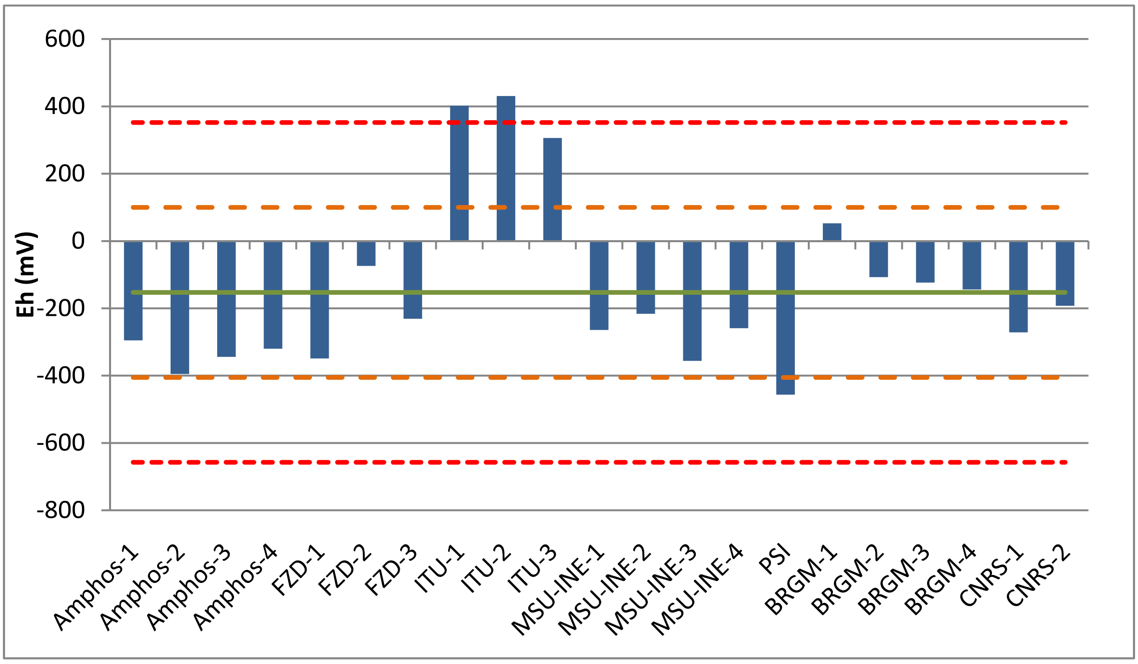


Figure 1.-Results obtained for sample REF 1 Fe a.
Lines represent average value (green), ±SD (orange) and ±2SD (red)

The box-whisker plot of all the replicates indicated that the three positive values of Eh from ITU were outliers. Once these values were removed the average value and standard deviation were -241 ± 127 mV.

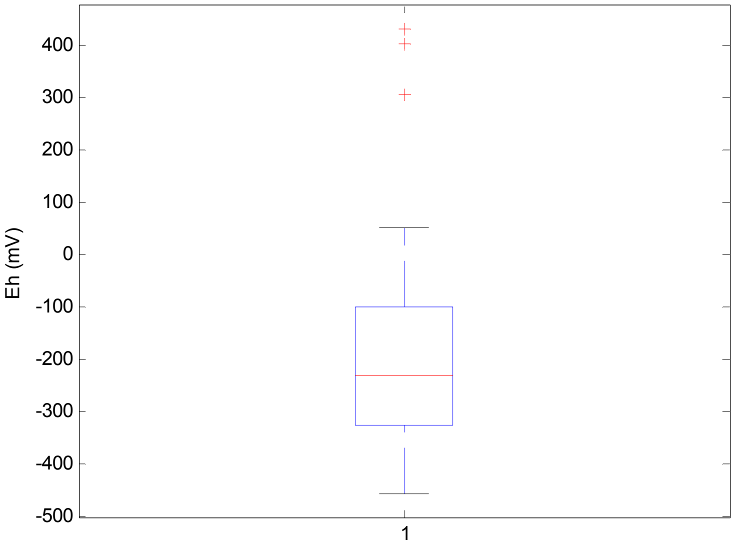


Figure 2.- Box-whisker plot of the results obtained for sample REF 1 Fe a.

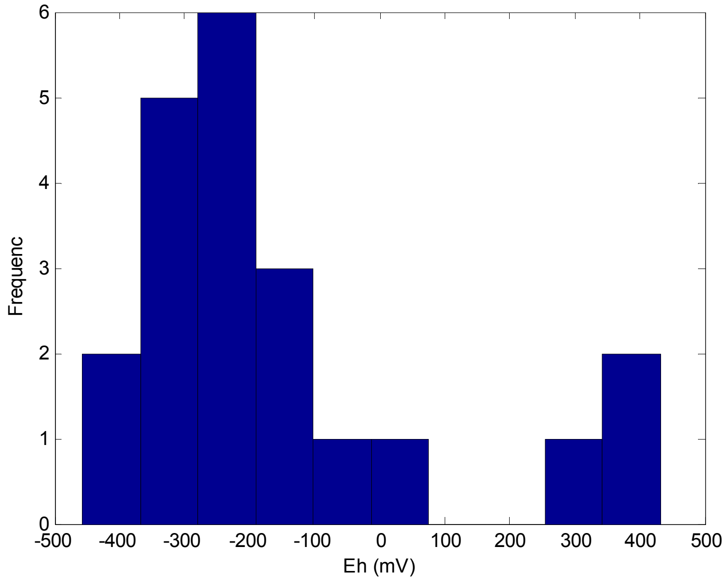


Figure 3.- Frequency histogram of the results obtained for sample REF 1 Fe a.

3.1.2 REF 1 Fe b

The replicate measurements for sample REF 1 Fe b can be seen in Table 2 and Figure 4.

Table 2.- Summary of the results obtained for sample REF 1 Fe b

Institution	**Method/Replicate**	**Eh (mV)**
Amphos		-283
FZD	Suspension	-307
	Filtrate	-87.4
	Supernatant	-93.8
PSI		-73.8
CTH	1	38
	2	6
	3	27
	4	41
IPL		-33
BRGM	Pt	-63.5
	Au	-61.34
	GC	-89.11
	Pyr	-59.17
	Pt disc	-67.7
CNRS	Amperometric: Pt UME glass	-113.6
	Amperometric: Pt UME glass	-166
	Amperometric: Pt UME glass	-350
	Potentiometric: Pt RDE	-352.6
	Potentiometric: Pt RDE	-96.1
	Potentiometric: Pt RDE	-173.1
Statistics	**Average**	-112
	SD	120
	RSD (%)	107
	Median	-87.4

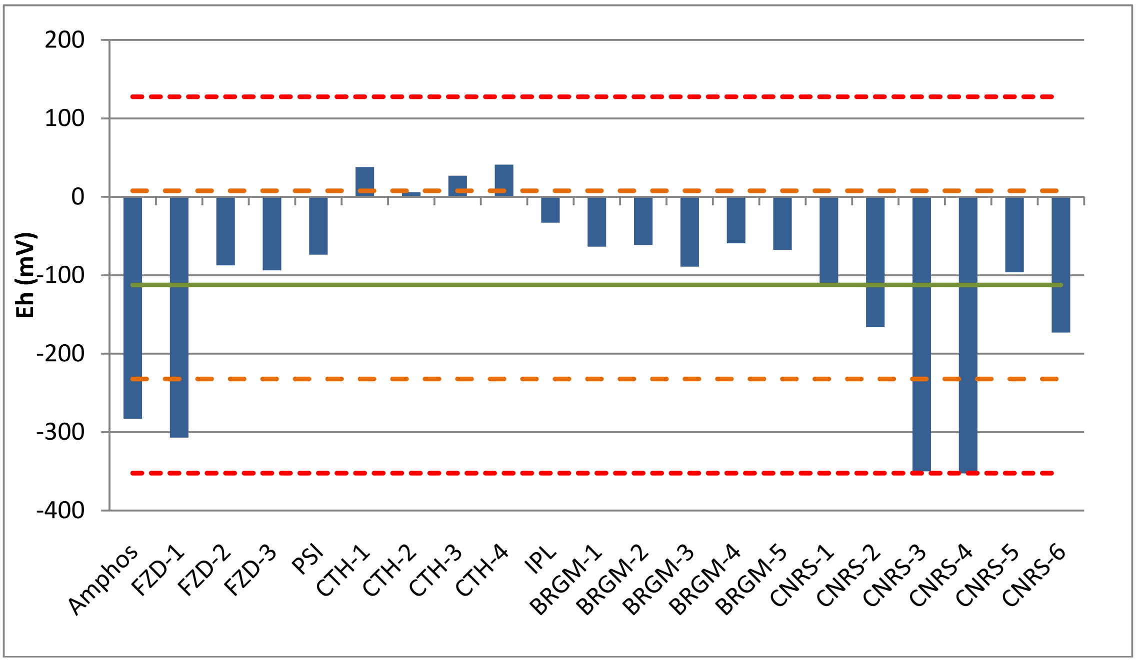


Figure 4.-Results obtained for sample REF 1 Fe b.
Lines represent average value (green), SD (orange) and 2SD (red)

The results ranged from -353 to +38 mV. The Box-plot indicates that the two replicates CNRS-3 and 4 could be outliers. As it can be seen in the frequency histogram the replicates do not follow a normal distribution, however most of the results gather around -100 and -50 mV.

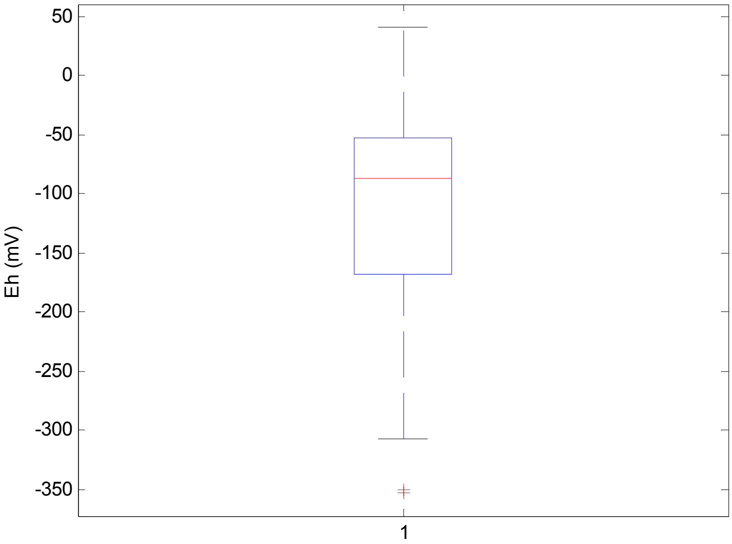


Figure 5.-Box-whisker plot of the results obtained for sample REF 1 Fe b.

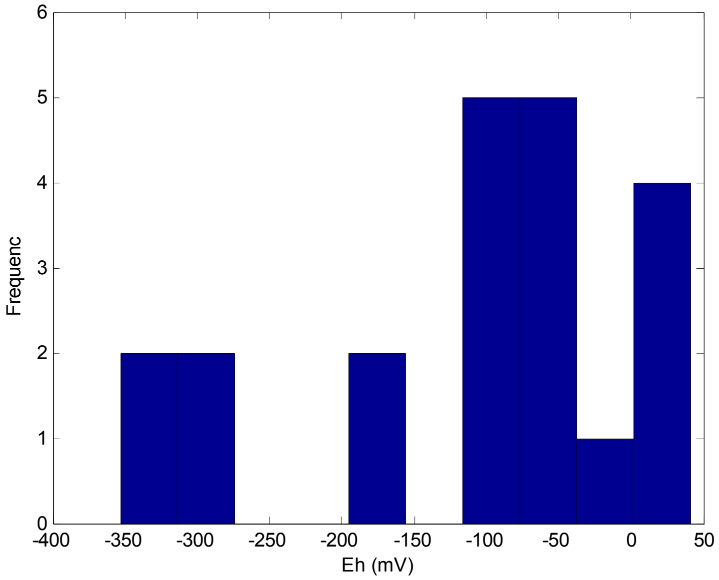


Figure 3.-Fequency histogram of the results obtained for sample REF 1 Fe b.

3.1.3 REF 1 (II/III) a

A total of 34 values were obtained for sample REF 1 (II/III) a. A summary of the values, as well as basic statistics can be seen in Table 3 and Figure 7.

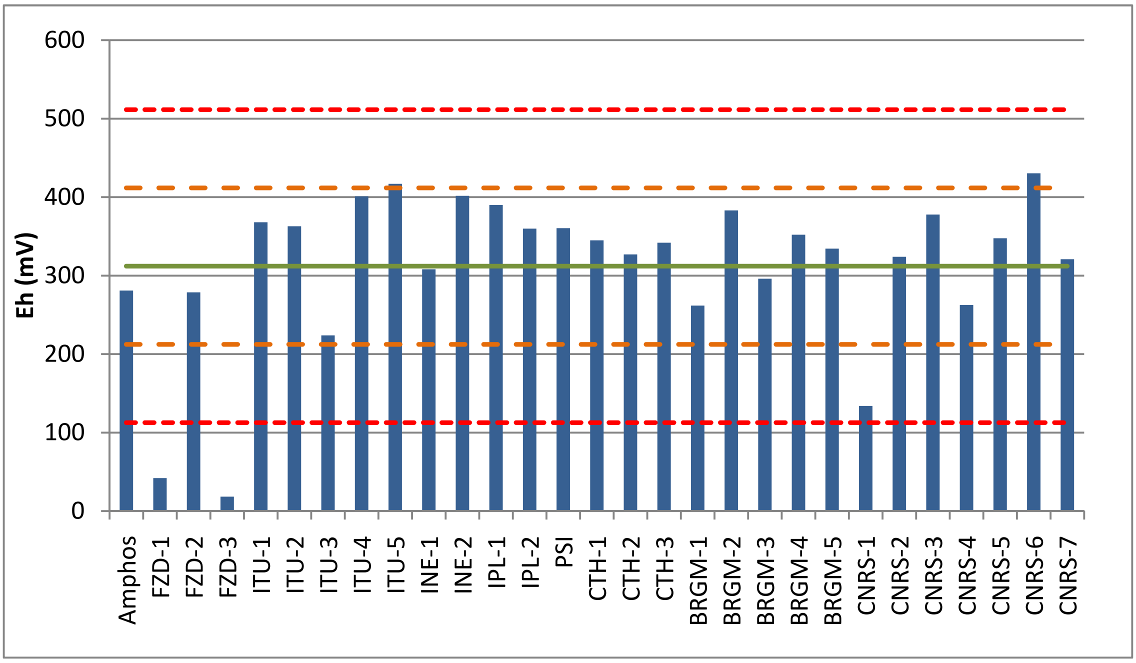


Figure 7.-Results obtained for sample REF 1 (II/III) a.
Lines represent average value (green), ±SD (orange) and ±2SD (red)

Table 3.- Summary of the results obtained for sample REF 1 (II/III) a

Institution	**Method/Replicate**	**Eh (mV)**
Amphos		281
FZD	Suspension	42
	Filtrate	278.7
	Supernatant	18.5
ITU	Comb Pt Stirred	368
	Comb Pt Static	363
	Comb Au Stirred	224
	RHE Com Pt O stirred	401
	RHE Com Pt O static	417
INE	Comb Pt	308.2
	Single Pt	401.8
IPL	1	390
	2	360
PSI		360.5
CTH	1	345
	2	327
	3	342
BRGM	Pt	261.8
	Au	383.11
	GC	296
	P r	352.19
	Pt disc	334.4
CNRS	Amperometric: Pt UME glass	134
	Amperometric: Pt UME glass	324
	Potentiometric: Pt RDE	377.8
	Potentiometric: Pt RDE	262.6
	Potentiometric: Pt RDE	347.6
	Potentiometric: Pt wire	430.4
	Potentiometric: Pt wire	321
FZD	Suspension	42
	Filtrate	278.7
	Supernatant	18.5
ITU	Comb Pt Stirred	368
	Comb Pt Static	363
Statistics	**Average**	312
	SD	100
	RSD (%)	32
	Median	342

As can be observed in Figure 7, only 2 samples, FDZ-1 and FDD-2, fell outside the interval of 2SD. The Box-whisker plot of the results (Figure 8) as well as the frequency histogram confirm that these two samples in addition to sample CNRS-1 behave as outliers.

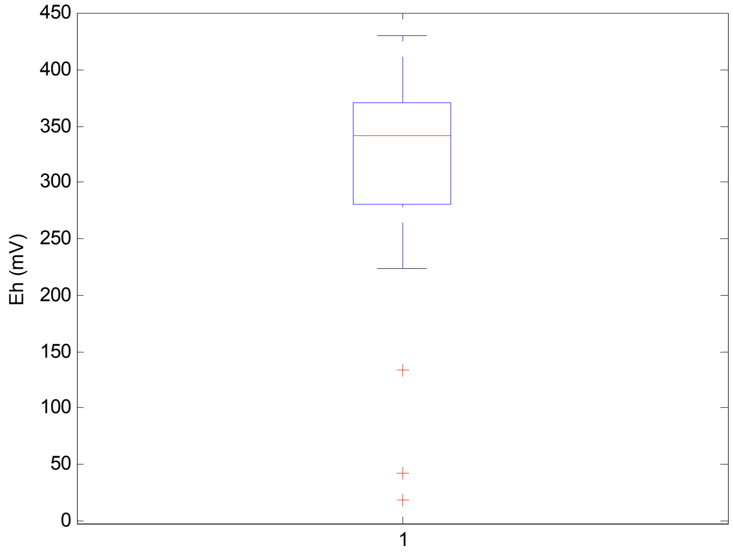


Figure 8.-Box-whisker plot of the results obtained for sample REF 1 (II/III) a.

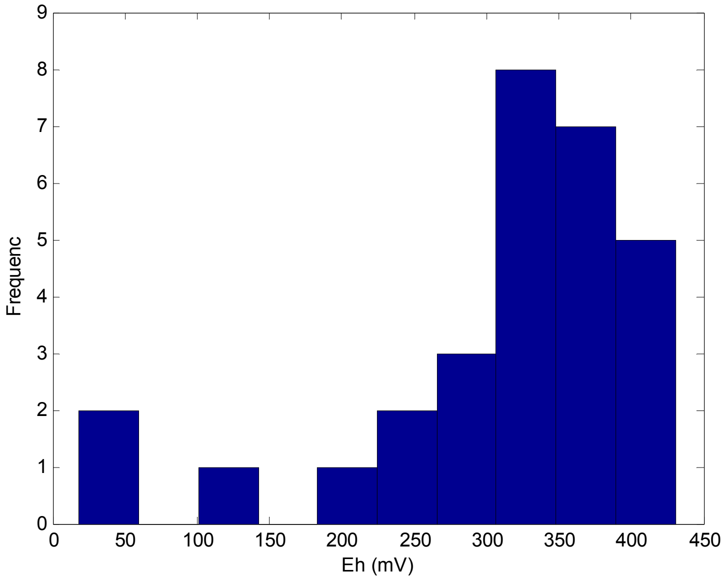


Figure 9.- Frequency histogram of the results obtained for sample REF 1 (II/III) a.

Once samples FDZ-1, FDD-2, and CNRS-1 are removed from the set, the resulting average value and SD are 341 ± 52 mV.

3.1.4 REF 1 (II/III) c

Table 4.- Summary of the results obtained for sample REF 1 (II/III) c

Institution	**Method/Replicate**	**Eh (mV)**
FZD	Suspension	698.3
	Filtrate	684.5
	Supernatant	451.9
ITU	Comb Pt Stirred	710
	Comb Pt Static	705
	Comb Au Stirred	698
INE	Comb Pt	686.1
	Single Pt	677
PSI		694
BRGM	Pt	576.4
	Au	691.05
	GC	649.8
	P r	643
	Pt disc	697.21
GRS	Comb Pt	714.02
	UV	704.8
CNRS	Amperometric: Pt UME glass	694
	Amperometric: Pt UME glass	702
	Potentiometric: Pt RDE	704
	Potentiometric: Pt RDE	704.7
Statistics	**Average**	674
	SD	61
	RSD (%)	9.0
	Median	696

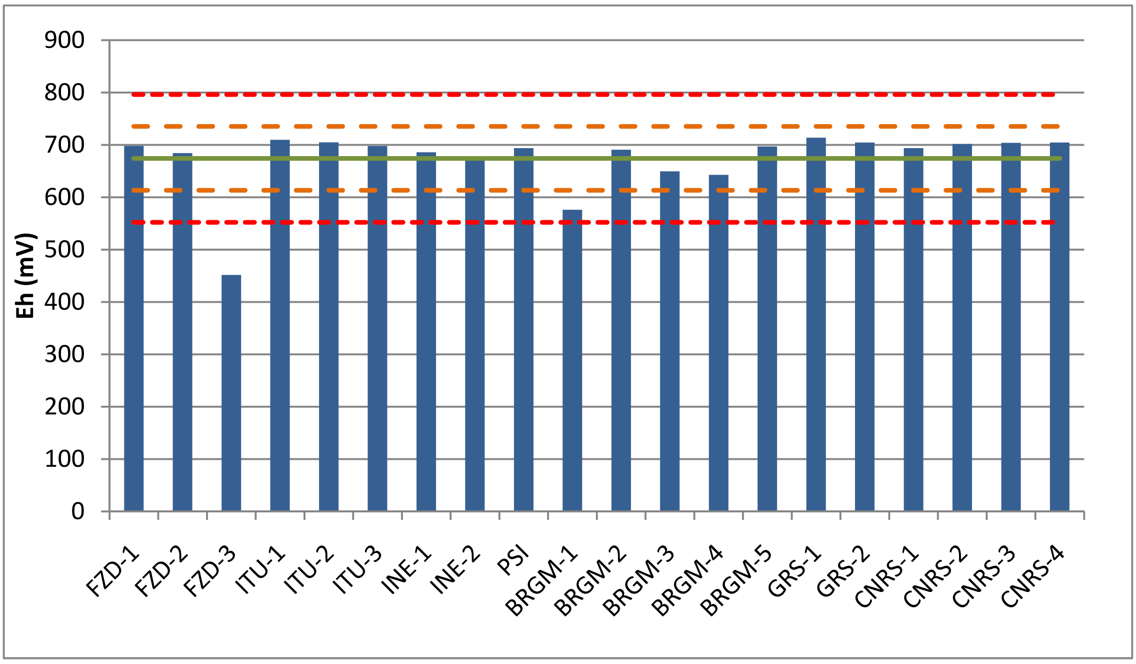


Figure 10.-Results obtained for sample REF 1 (II/III) c.
Lines represent average value (green), ± SD (orange) and ± 2SD (red)

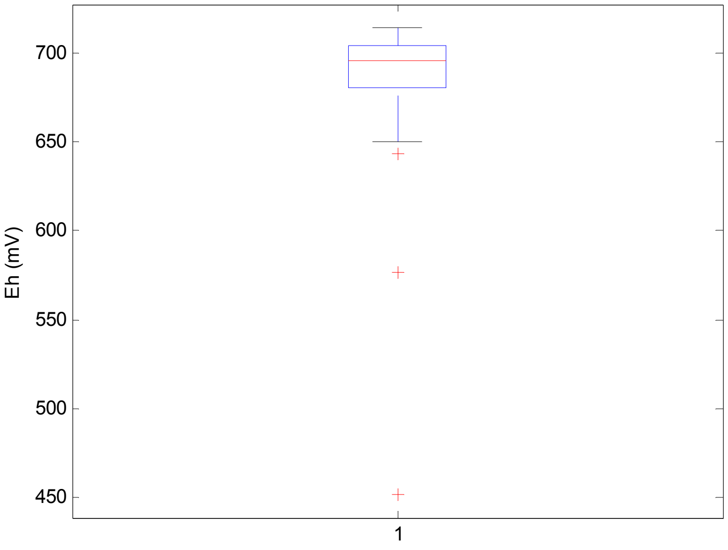


Figure 11.- Box-whisker plot of the results obtained for sample REF 1 (II/III) c.

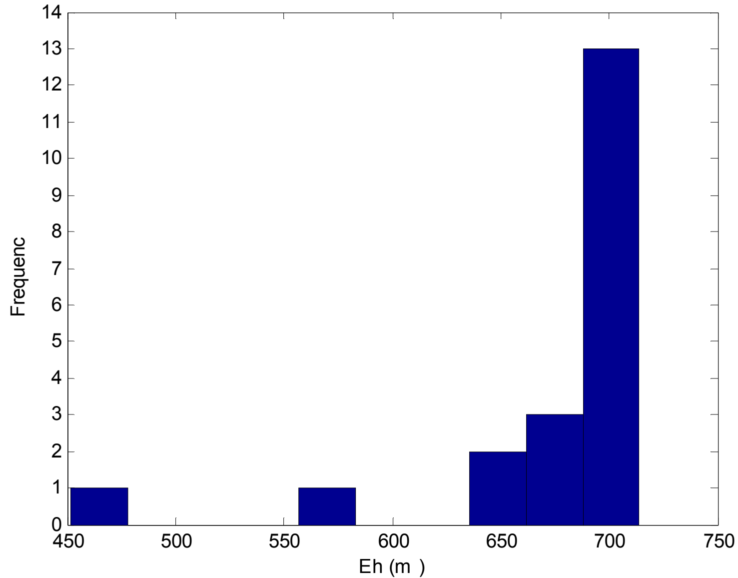


Figure 12.- Frequency histogram of the results obtained for sample REF 1 (II/III) c.

3.1.5 Suspension of Mackinawite a and b

As it can be seen from the summary Table 5 and Figure 13, samples are distributed in a quite narrow interval of results, the only exception being sample FDZ-2 (Filtrate), which can be considered an outlier according to the Box-whisker-plot (Figure 14).

Table 5.- Summary of the results obtained for sample Sus-Mack-a

Institution	**Method/Replicate**	**Eh (mV)**
FZD	Suspension	-236
	Filtrate	18.4
	Supernatant	-152.7
PSI		-241.6
CNRS	Amperometric: Pt UME glass	-251
	Potentiometric: Pt RDE	-231.6
	Potentiometric: Pt RDE	-237.3
Statistics	**Average**	-190
	SD	98
	RSD (%)	51
	Median	-236

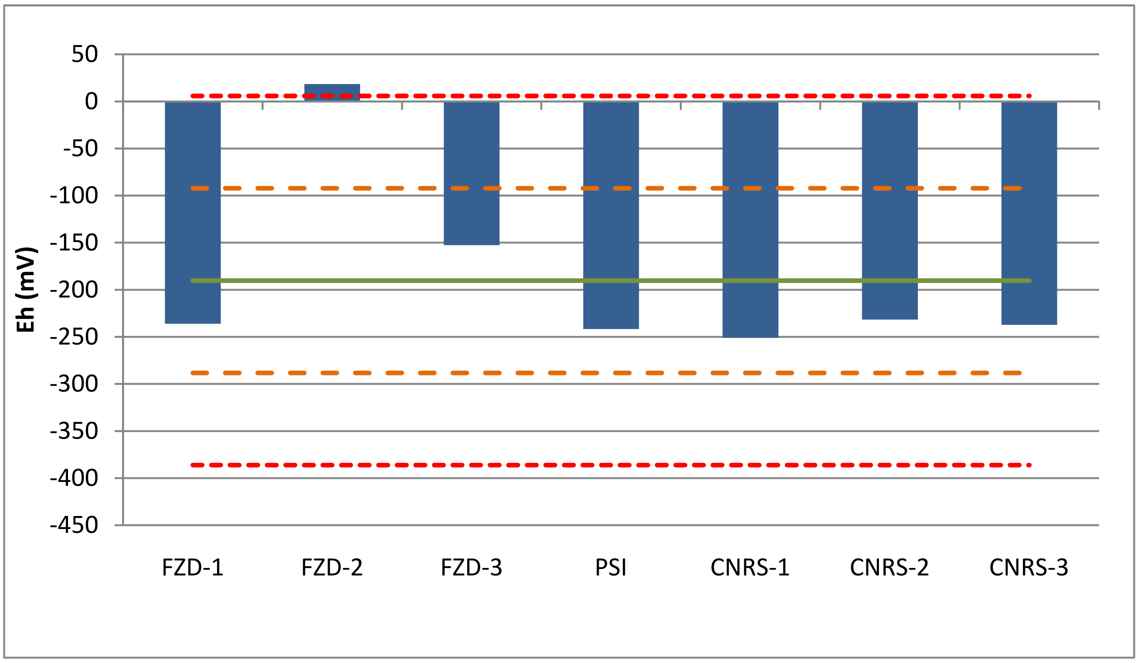


Figure 13.-Results obtained for sample Sus-Mack-a.
Lines represent average value (green), ± SD (orange) and ± 2SD (red)

The histogram (Figure 15) indicates that the measurement of Eh in the supernatant and the filtrate give clearly different results from the direct measurement of the whole suspension. This would suggest that depending on the purpose of the study, measurement of the whole suspension, filtrate and/or supernatant could be recommended as they provide clearly different results.

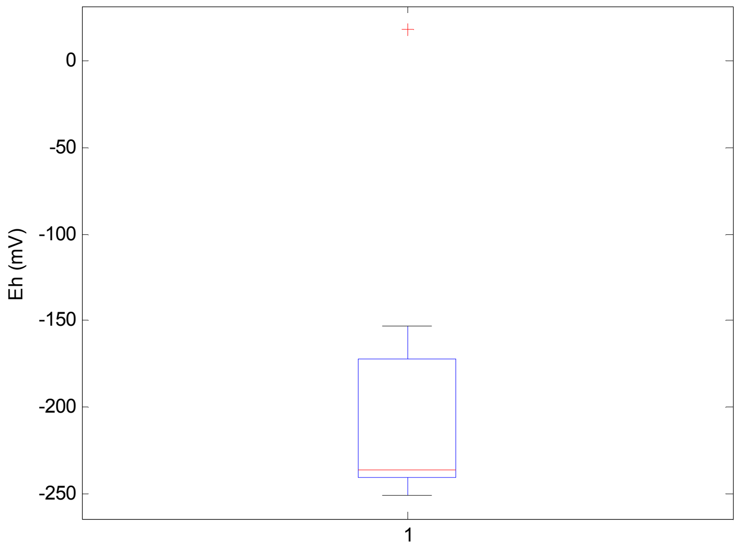


Figure 14.- Box-whisker plot of the results obtained for sample Sus-Mack-a

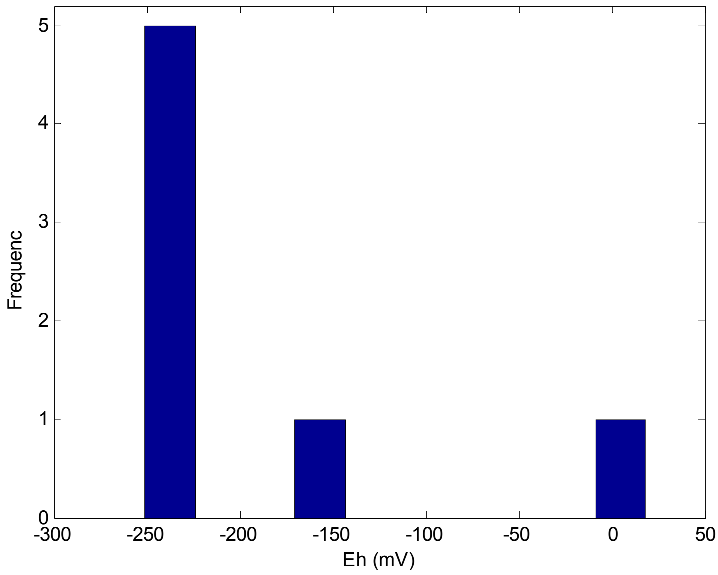


Figure 15.-Frequency histogram of the results obtained for sample Sus-Mack-a

Table 6 and Figure 16 summarise the results obtained for sample Sus-Mack b. As in the case of sample Sus-Mack-a, results from filtrate (FZD-2) clearly differs from the measurement of the whole suspension.

Table 6.- Summary of the results obtained for sample Sus-Mack-b

Institution	**Method/Replicate**	**Eh (mV)**
Amphos		-321
FZD	Suspension	-300.9
	Filtrate	-51.2
	Supernatant	-201.8
PSI		-297.9
BRGM	Pt	-142.6
	Au	-285.2
	GC	-253.5
	Pyr	-115.14
	Pt disc	-294.8
Statistics	**Average**	-226
	SD	94
	RSD (%)	41
	Median	-269

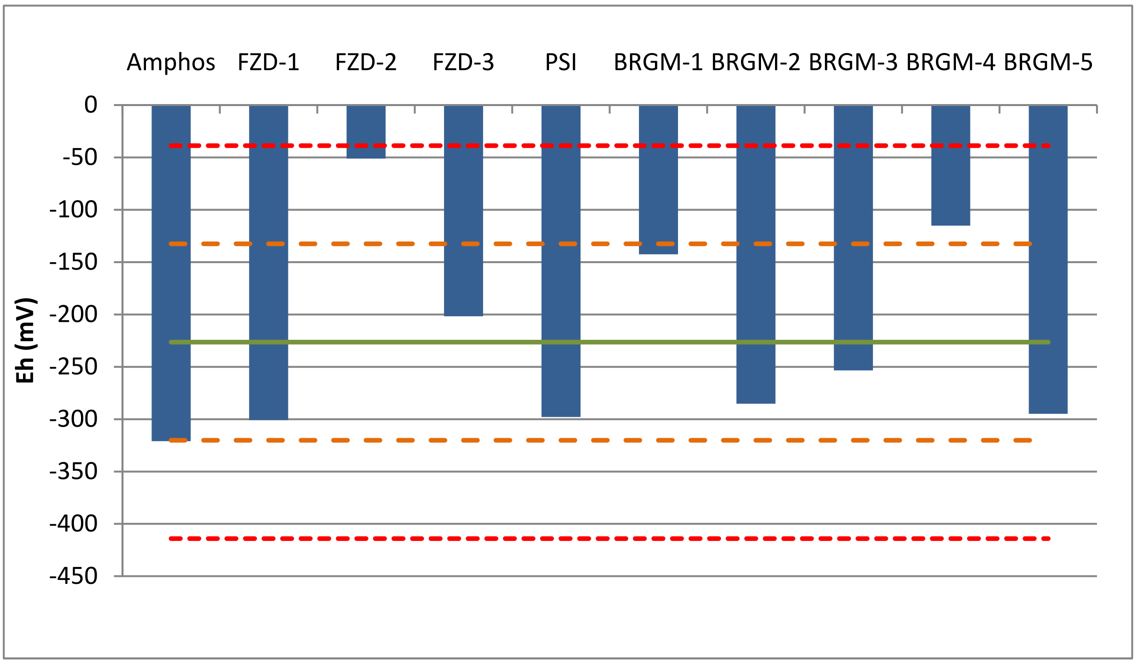


Figure 16.-Results obtained for sample Sus-Mack-b.
Lines represent average value (green), ±SD (orange) and ±2SD (red)

As can be observed in Figures 17 and 18, the results are distributed across a very wide range of Eh values rather evenly, therefore none of them could be considered an outlier. The relative standard deviation is approx. 40%. It is possible that the nature of the sample itself, being a suspension, would justify the spread of the results.

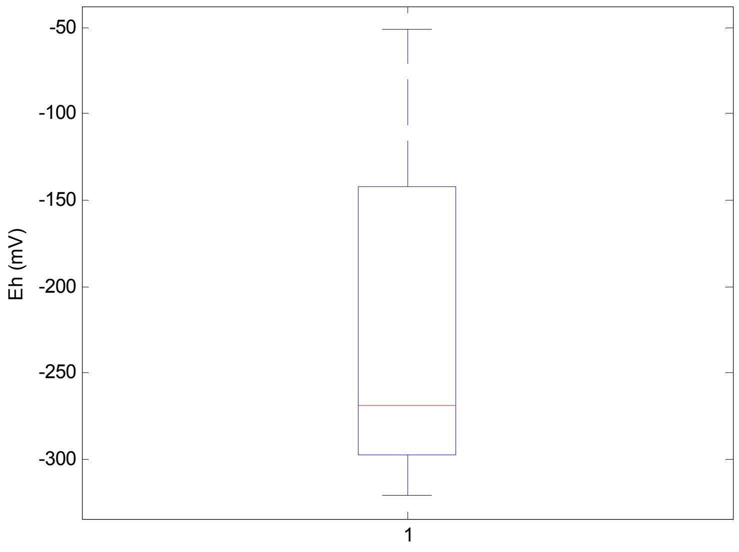


Figure 17.- Box-whisker plot of the results obtained for sample Sus-Mack-b

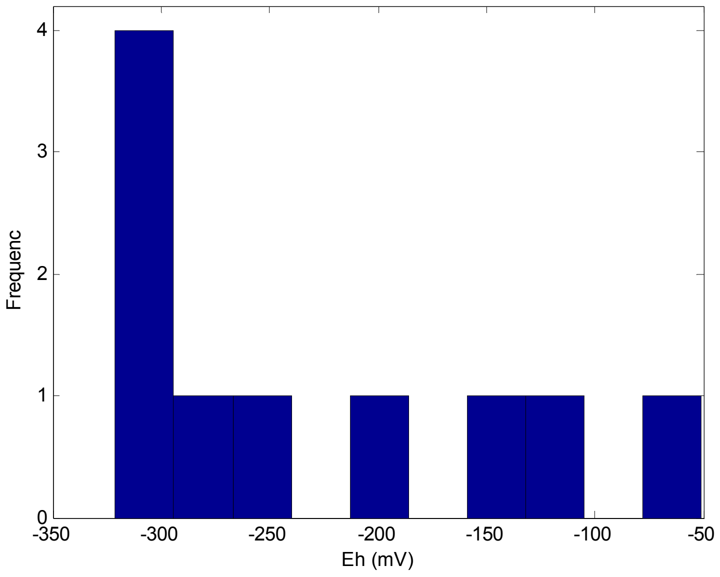


Figure 18.-Fequency histogram of the results obtained for sample Sus-Mack-b

3.1.6 Suspension of Magnetite a and b

As it can be observed in Table 7, and Figures 19 and 20, results are distributed across a very wide range, with a relative standard deviation that reaches 95%.

Table 7.- Summary of the results obtained for sample Sus-Magn-a

Institution	Method/Replicate	Eh (mV)
Amphos		46
FZD	Suspension	66
	Filtrate	96.3
	Supernatant	70
ITU	Comb Pt static	193
	Comb Pt stirred	118
	Comb Au stirred	217
PSI		114.5
CNRS	Amperometric: Pt UME glass	-101
	Potentiometric: Pt RDE	93.6
Statistics	**Average**	91
	SD	87
	RSD (%)	95
	Median	95

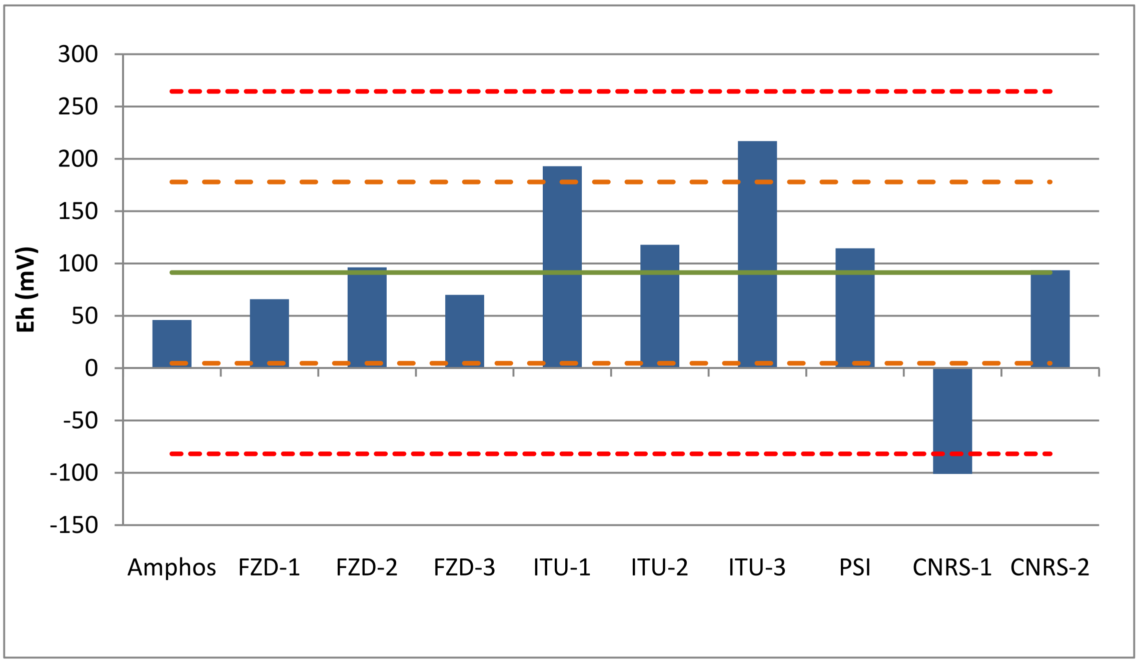


Figure 19.-Results obtained for sample Sus-Magn-a.
Lines represent average value (green), SD (orange) and 2SD (red)

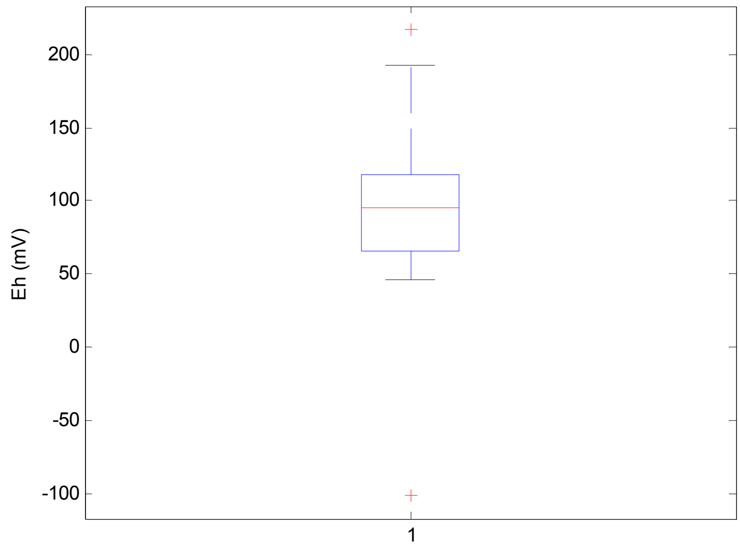


Figure 20.- Box-whisker plot of the results obtained for sample Sus-Magn-a

As can be concluded from the box-whisker plot for the results obtained by the amperometric method, the only negative potential from all the set of results, behaves as an outlier. Even after the removal of this value, the results are still very scattered (X ± SD = 113 ± 57, RSD %= 51) as observed also for other suspension samples. However, the frequency histogram (Figure 21) shows that the most frequent values distribute around + 95 mV.

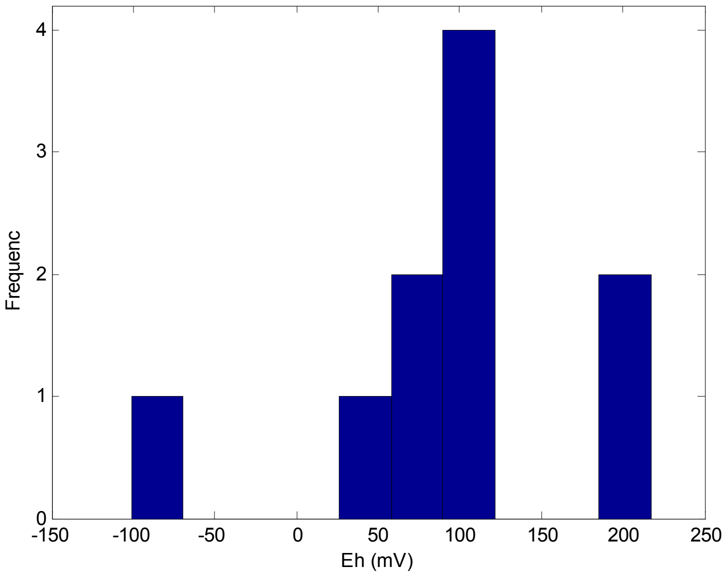


Figure 21.-Fequency histogram of the results obtained for sample Sus-Magn-a

Table 8 shows the results obtained for the suspension of Magnetite-b. Figures 22 and 23 indicate that the results are spread across a very wide range. The frequency histogram clearly shows that the results distribute around two values, one about -250 mV obtained for the suspensions (Table 8) and a higher value around -50 mV for the filtrate and supernatant. However, these conclusions should be taken with caution, due to the small number of replicates (n = 5). Once more, for this sample, the results illustrate how critical is the presence of the original solid for the measurements of the Eh of a suspension. Knowing this, the decision about filtering the sample before measurement, should be left to the researcher according to the objectives of the particular study.

Table 8.- Summary of the results obtained for sample Sus-Magn-b

Institution	**Method/Replicate**	**Eh (mV)**
Amphos		-269
FZD	Suspension	-272.3
	Filtrate	-47.2
	Supernatant	-48.6
PSI		-263
Statistics	**Average**	-180
	SD	121
	RSD (%)	67
	Median	-263

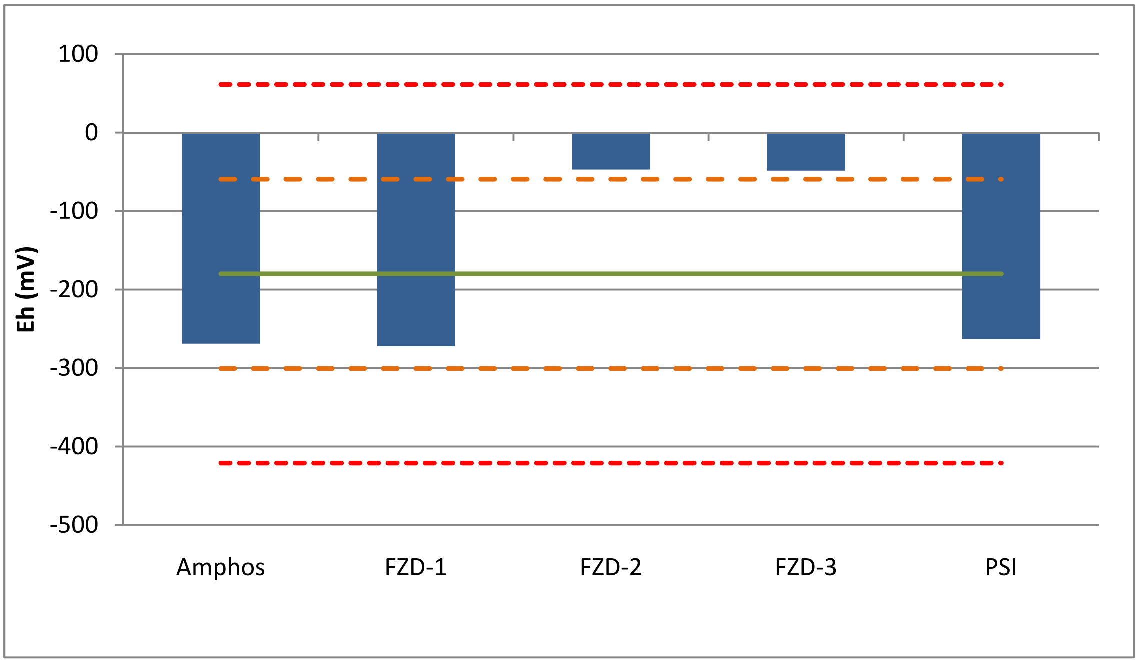


Figure 22.-Results obtained for sample Sus-Magn-b.
Lines represent average value (green), SD (orange) and 2SD (red)

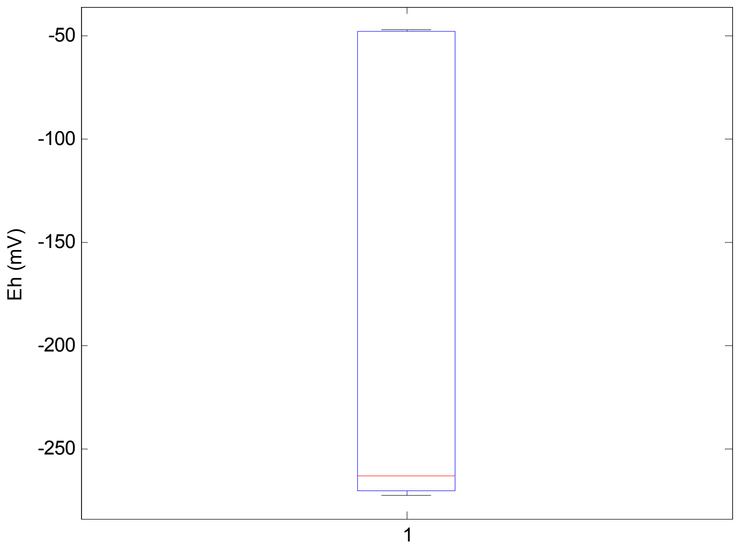


Figure 23.- Box-whisker plot of the results obtained for sample Sus-Magn-b

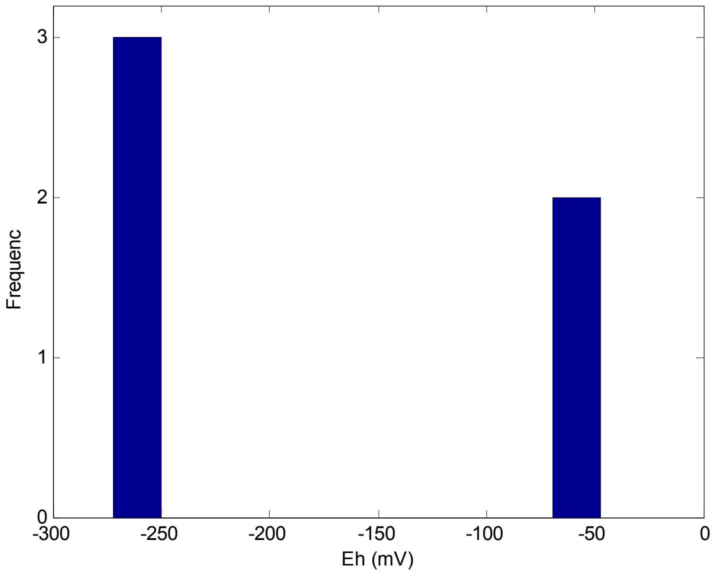


Figure 24.-Fequency histogram of the results obtained for sample Sus-Magn-b

3.2 Brine Fe systems (REF 2)

3.2.1 REF 2 Na a

Table 9 summarises the results obtained for sample REF 2 Na a. Replicates are rather scattered (Figure 25) with a relative standard deviation around 50%. However, the box-whisker plot (Figure 26) did not point out any of the samples as outliers. The most frequently obtained values gather around + 350 mV, as observed in the frequency histogram (Figure 27).

Table 9.- Summary of the results obtained for sample REF 2 Na a

Institution	Method/Replicate	Eh (mV)
BRGM	Pt	333.98
	Au	374.87
	GC	342.1
	P r	115.7
	Pt disc	341.6
PSI		350
CNRS	Amperometric: Pt UME epo	48
	Amperometric: Pt UME epo	155
	Potentiometric: Pt RDE	216.1
	Potentiometric: Pt RDE	512.2
	Potentiometric: Pt wire	305.2
Statistics	**Average**	281
	SD	134
	RSD (%)	48
	Median	334

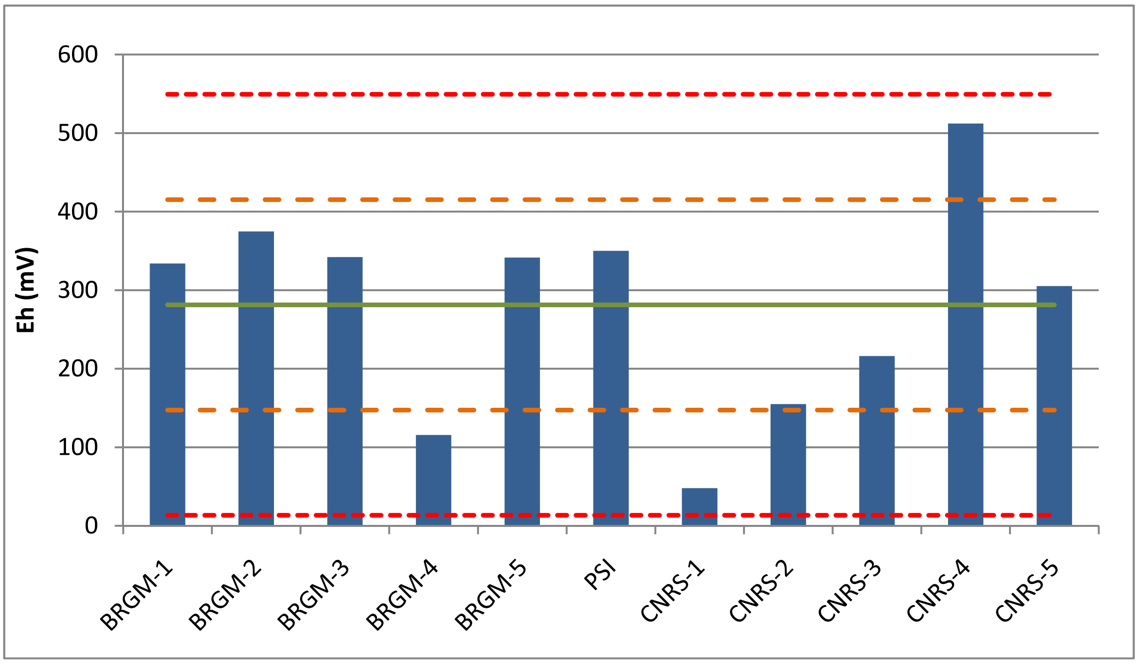


Figure 25.-Results obtained for sample REF 2 Na a.
Lines represent average value (green), SD (orange) and 2SD (red)

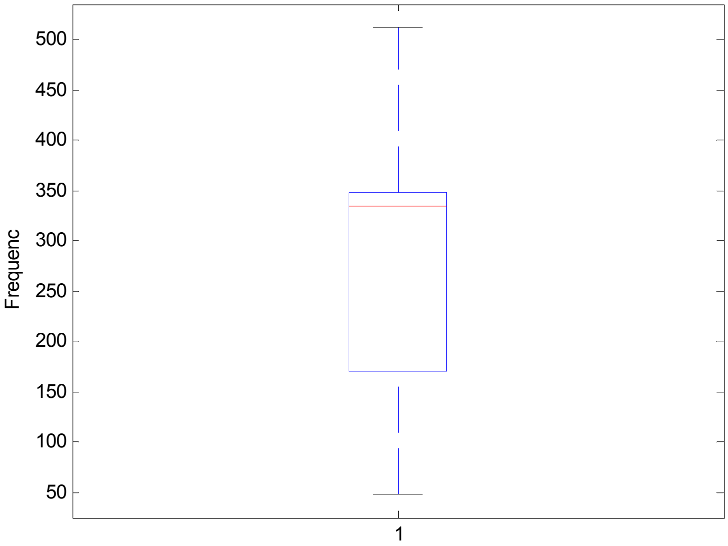


Figure 26.- Box-whisker plot of the results obtained for sample REF 2 Na a

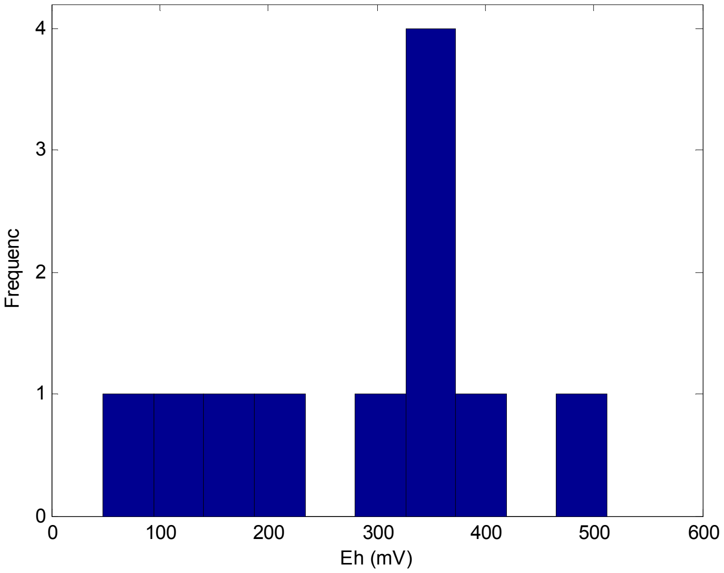


Figure 27.-Fequency histogram of the results obtained for sample REF 2 Na a

3.2.2 REF 2 Na b

Results for sample REF 2 Na b (Table 10) show an even wider scattering than sample Na a, with a relative standards deviation that reached almost 200%. Replicates ranged from -117 mV to +292 mV, however they did not follow a normal distribution as can be observed in Figure 30. Due to the scattering of the results, none of them can be consider as outliers (Figure 29).

Table 10.- Summary of the results obtained for sample REF 2 Na b

Institution	Method/Replicate	Eh (mV)
Amphos		66
BRGM	Pt	151.74
	Au	-137
	GC	-85.22
	P r	71.23
	Pt disc	-117
PSI		107.7
CNRS	Amperometric: Pt UME epo	111
	Amperometric: Pt UME epo	-9.6
	Potentiometric: Pt RDE	170.8
	Potentiometric: Pt RDE	162.5
	Potentiometric: Pt RDE	292.9
	Potentiometric: Pt wire	69.1
Statistics	**Average**	65.7
	SD	125
	RSD (%)	190
	Median	71

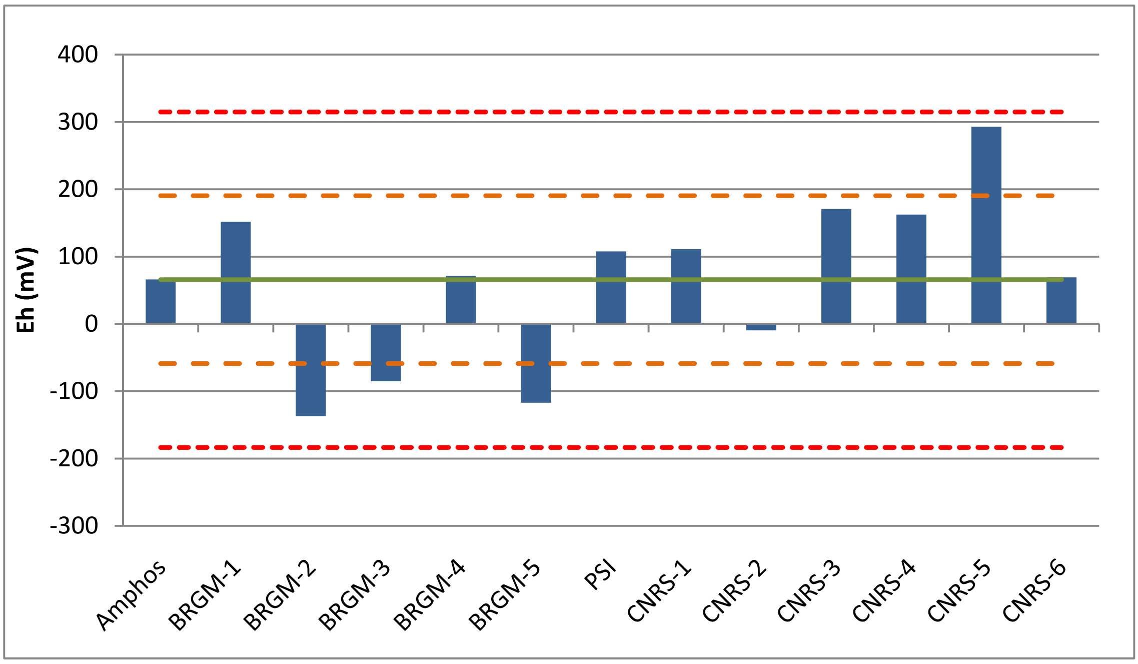


Figure 28.-Results obtained for sample REF 2 Na b.
Lines represent average value (green), ± SD (orange) and ± 2SD (red)

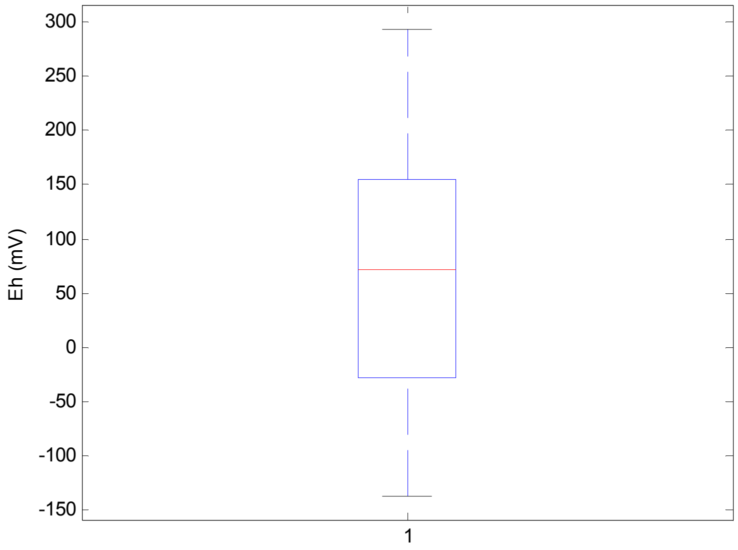


Figure 29.- Box-whisker plot of the results obtained for sample REF 2 Na b

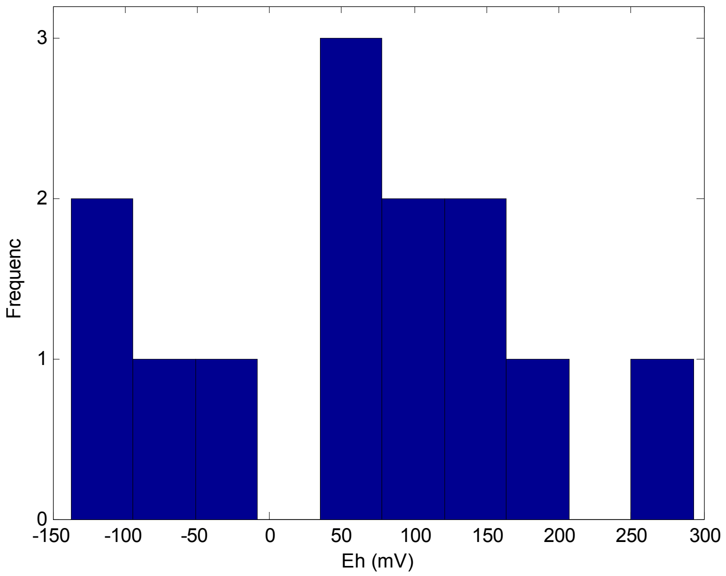


Figure 28.-Frequency histogram of the results obtained for sample REF 2 Na b

3.2.3 REF 2 Na c

Table 11 and Figure 31 summarise the results and basic statistics for sample REF2 Na c.

Table 11.- Summary of the results obtained for sample REF 2 Na c

Institution	**Method/Replicate**	**Eh (mV)**
BRGM	Pt	224.9
	Au	675.4
	GC	684.3
	Pyr	664.9
	Pt disc	689.6
GRS*	Comb Pt	702.4
	UV	691.9
CNRS	Amperometric: Pt UME epoxy	695
	Potentiometric: Pt RDE	692
Statistics	**Average**	636
	SD	154
	RSD (%)	24
	Median	690

For comparison purposes, only the results at the original ionic strength have been considered

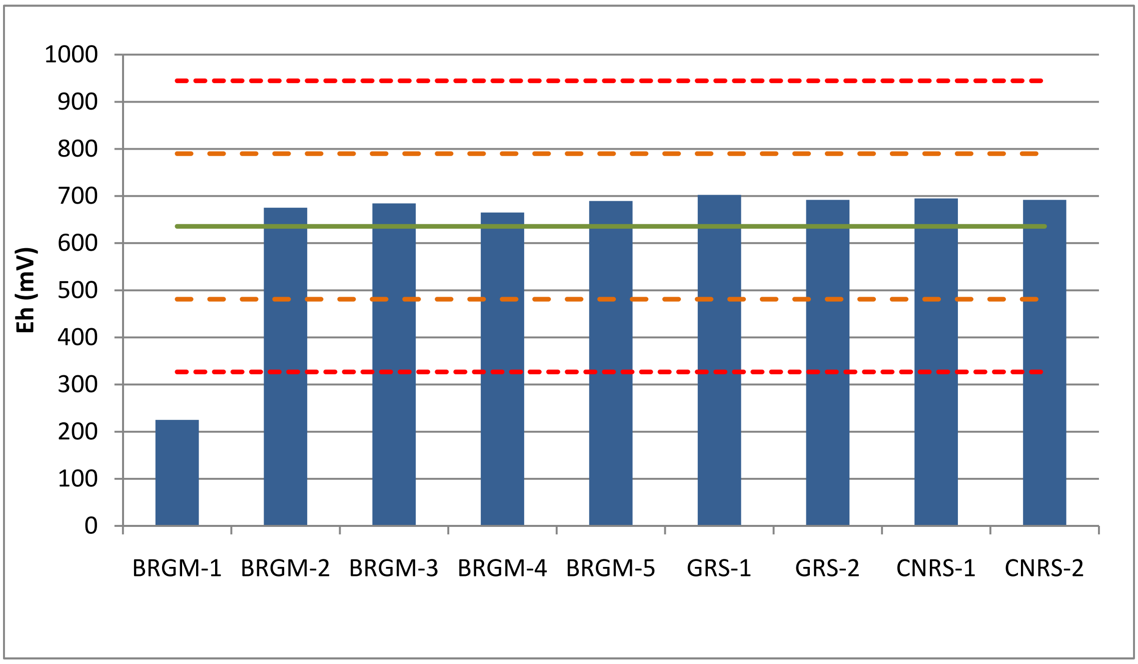


Figure 31.-Results obtained for sample REF 2 Na c.
Lines represent average value (green), ±SD (orange) and ±2SD (red)

The box-whisker plot (Figure 32) suggests that the replicate BGRM-1 (with Pt electrode) is an outlier. After the removal of this value, the average and standard deviation would be 687 ± 12 (% RSD ca. 2%).

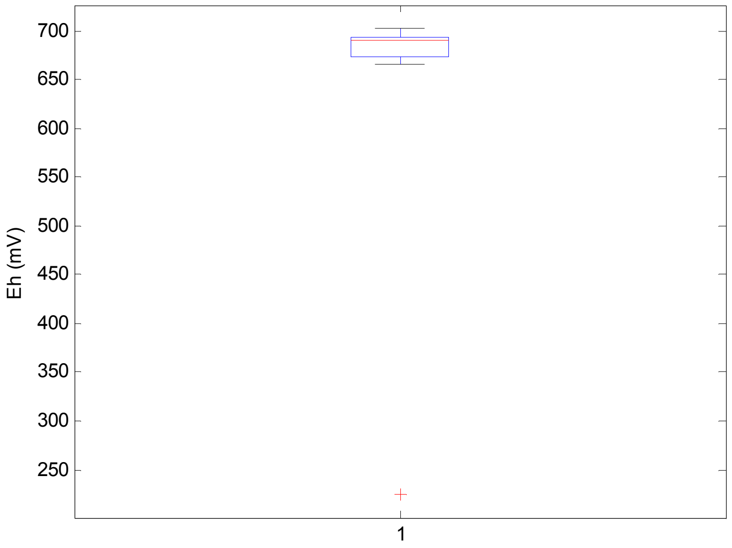


Figure 32.- Box-whisker plot of the results obtained for sample REF 2 Na c

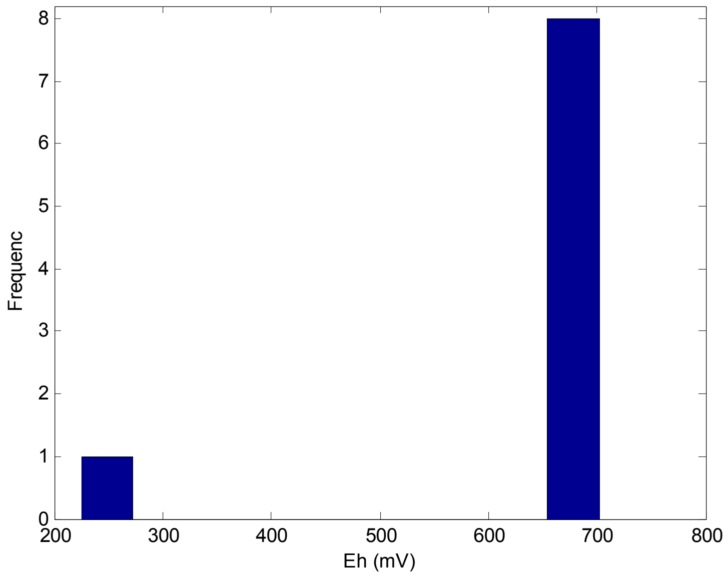


Figure 33.-Fequency histogram of the results obtained for sample REF 2 Na c

3.2.4 REF 2 Mg b

Table 12 and Figure 34 show the results obtained from sample REF2 Mg b (6 replicates). The measurements ranged from +84 to + 242 mV, with a relative standard deviation of ca. 40%.

Table 12.- Summary of the results obtained for sample REF 2 Mg b

Institution	**Method/Replicate**	**Eh (mV)**
BRGM	Pt	183.5
	Au	242.2
	GC	140.5
	Pyr	298.8
	Pt disc	83.8
PSI		203.4
Statistics	**Average**	192
	SD	75
	RSD (%)	39
	Median	193

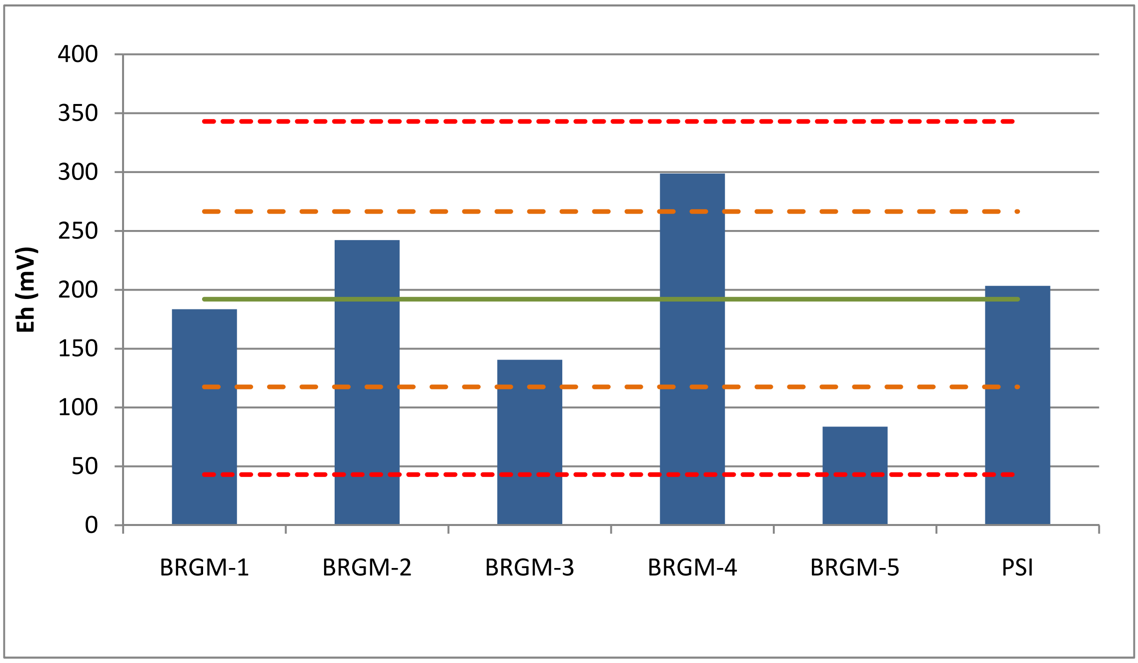


Figure 34.-Results obtained for sample REF 2 Mg b.
Lines represent average value (green), ±SD (orange) and ±2SD (red)

Due to the small number of replicates (n=6) and the wide spread of results, none of them can be treated as outliers (Figures 35 and 36).

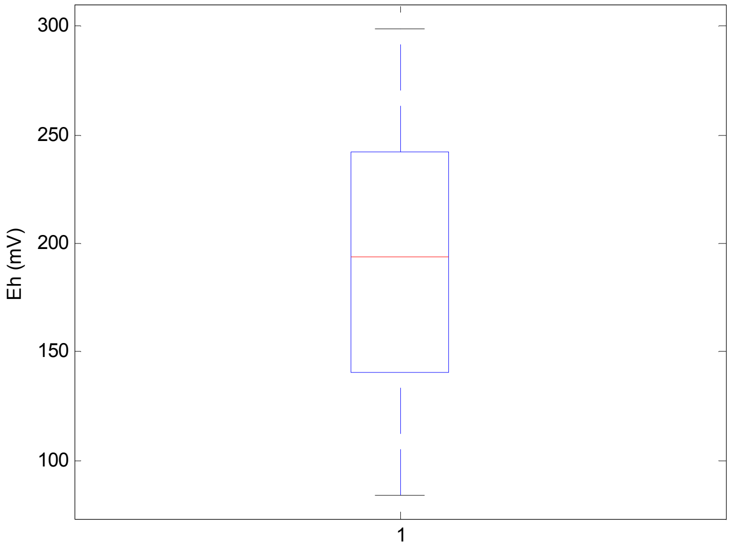


Figure 35.- Box-whisker plot of the results obtained for sample REF 2 Mg b

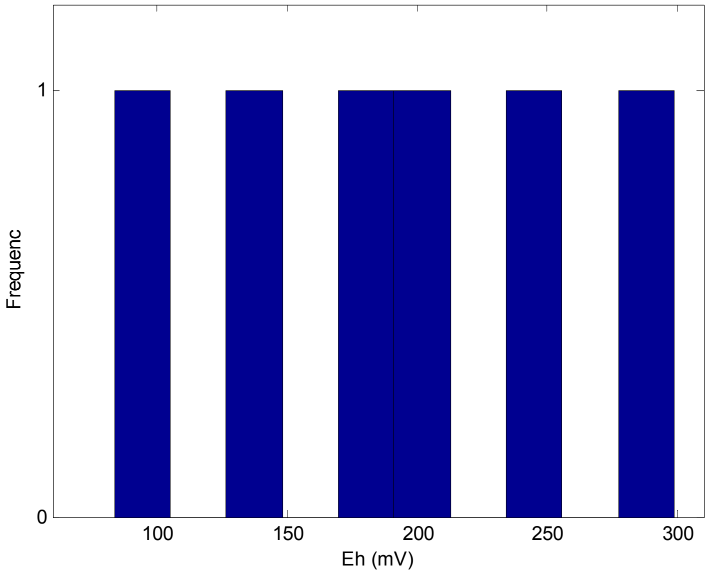


Figure 36.-Fequency histogram of the results obtained for sample REF 2 Mg b

3.2.5 REF 2 Mg c

Table 13 and Figure 37 show the replicate measurements (n = 7) of sample REF 2 Mg c.

Table 13.- Summary of the results obtained for sample REF 2 Mg c

Institution	Method/Replicate	Eh (mV)
BRGM	Pt	220.7
	Au	617.8
	GC	684.5
	Pyr	642.7
	Pt disc	677
GRS*	Comb Pt	692.3
	UV	675.7
Statistics	**Average**	602
	SD	170
	RSD (%)	28
	Median	676

* For comparison purposes, only the results at the original ionic strength have been considered

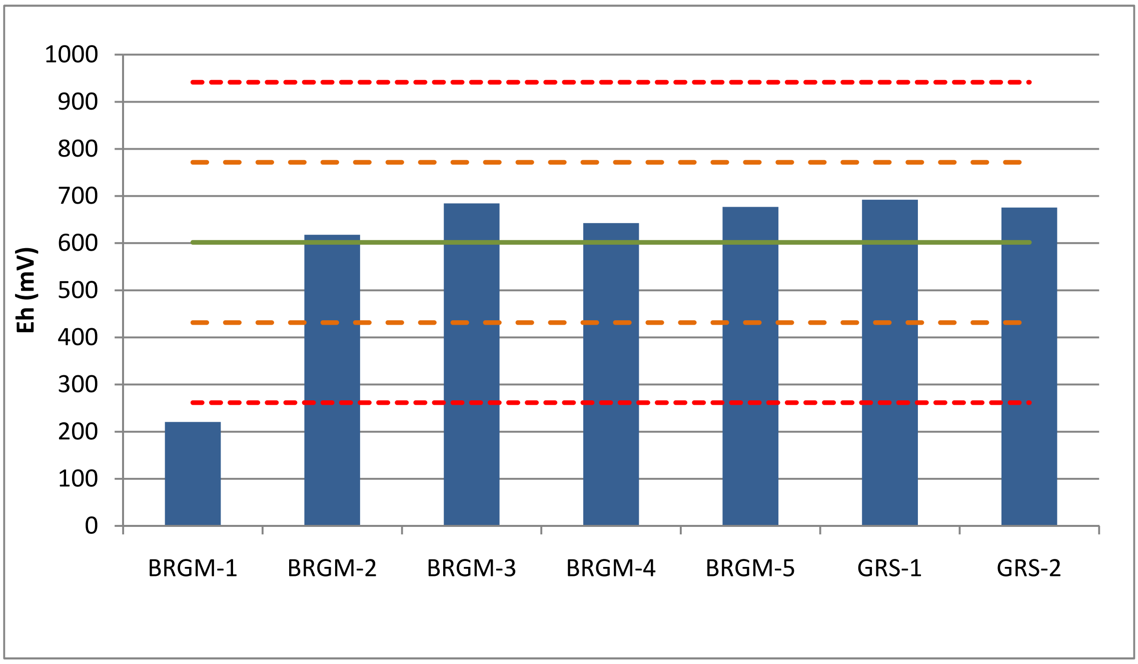


Figure 37.-Results obtained for sample REF 2 Mg c.
Lines represent average value (green), ± SD (orange) and ± 2SD (red)

The box-plot (Figure 38) and frequency histogram suggest that the frits replicate result from BGRM obtained with the Pt electrode behaves as an outlier. After the removal of this replicate from the results set, the average value and standard deviation are + 665 ± 29 mV, and the relative standard deviation is now approx. 4% (compared with the previous value, around 28% in Table 13)

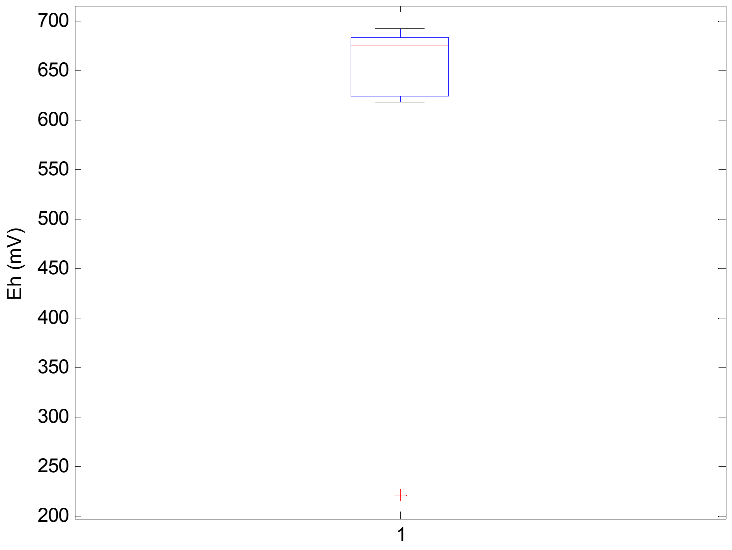


Figure 38.- Box-whisker plot of the results obtained for sample REF 2 Mg c

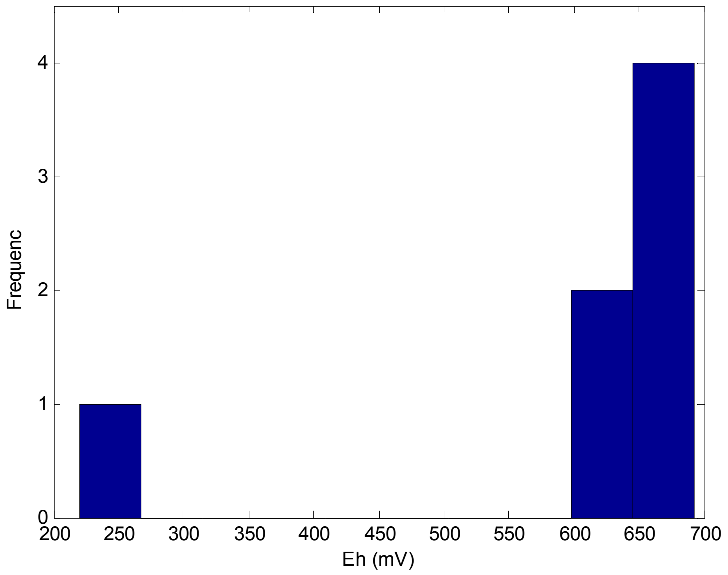


Figure 39.- Frequency histogram of the results obtained for sample REF 2 Mg c

3.2.6 REF 2 Ca b

Table 14 and Figure 40 summarise the results obtained for sample REF 2 Ca b (n=7). As it can be observed in Figure 40, replicates range across a rather wide interval from -128 mV to + 155 mV. Despite the huge relative standard deviation (ca. 360%), none of the results could be described as outliers (Figure 41 and 42), because of the low number of results and their spread.

Table 14.- Summary of the results obtained for sample REF 2 Ca b

Institution	**Method/Replicate**	**Eh (mV)**
Amphos		93
BRGM	Pt	155
	Au	-126
	GC	-56.9
	P r	102.3
	Pt disc	-77.5
PSI		103.7
ULough		34
Statistics	**Average**	28.4
	SD	103
	RSD (%)	361
	Median	63.5

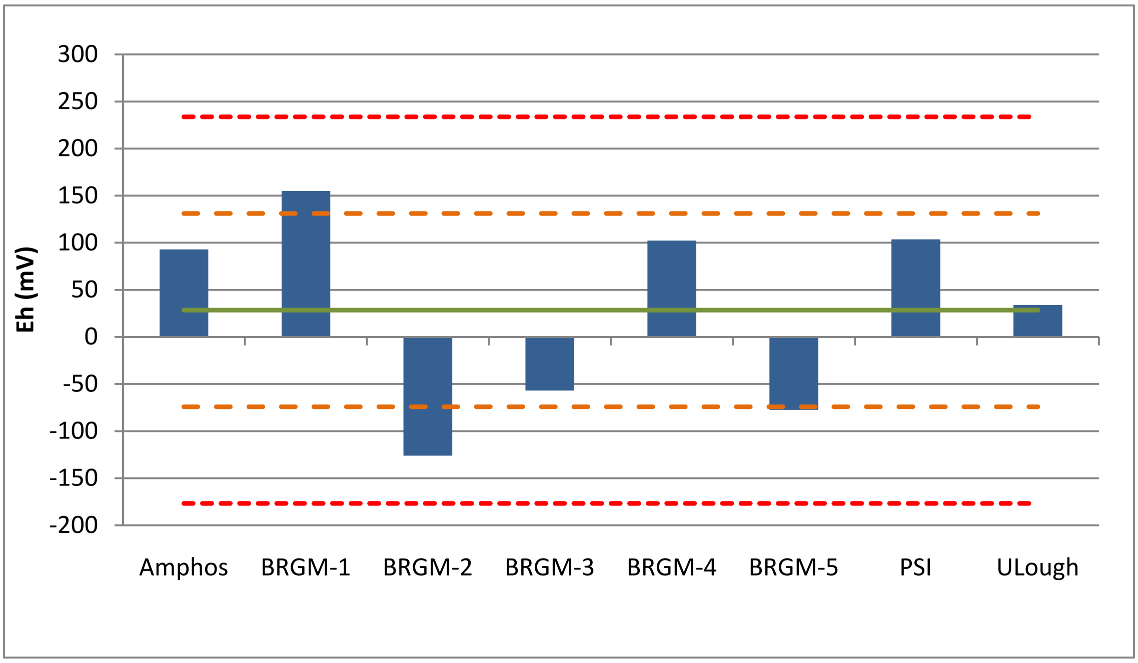


Figure 40.-Results obtained for sample REF 2 Ca b.
Lines represent average value (green), SD (orange) and 2SD (red)

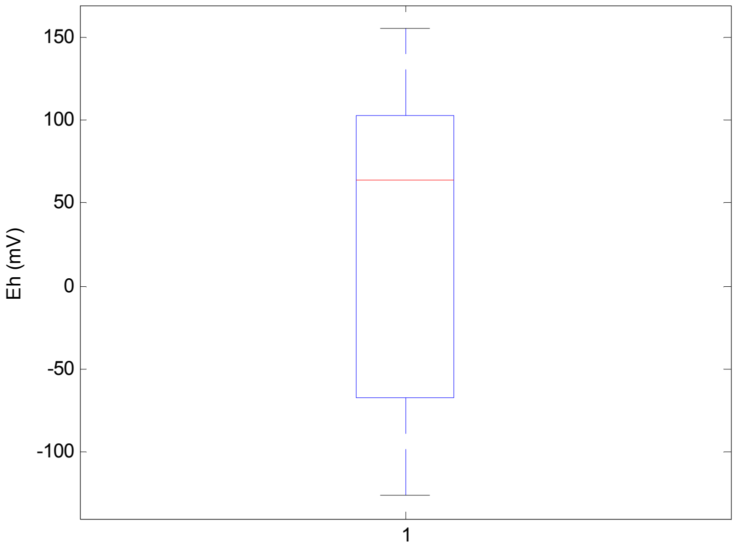


Figure 41.- Box-whisker plot of the results obtained for sample REF 2 Ca b

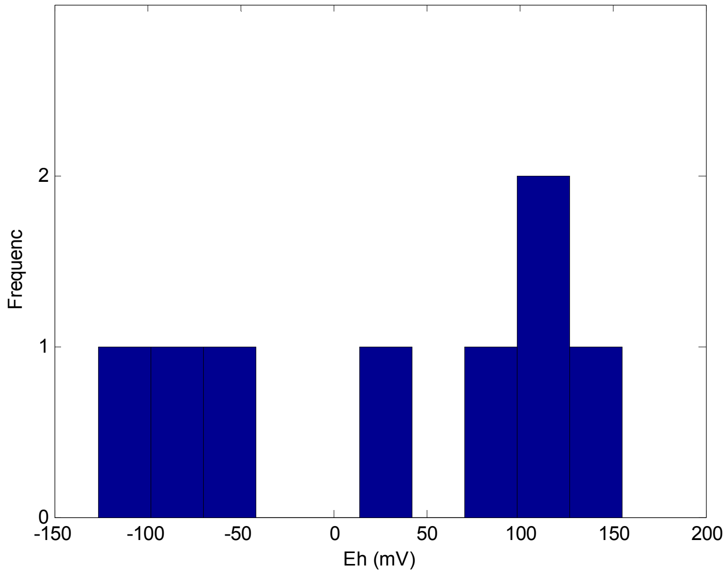


Figure 42.-Fequency histogram of the results obtained for sample REF 2 Ca b

3.2.7 REF 2 Ca c

Table 15 shows the results for sample REF2 Ca c, represented in Figure 43.

Table 15.- Summary of the results obtained for sample REF 2 Ca c

Institution	Method/Replicate	Eh (mV)
BRGM	Pt	279
	Au	694.2
	GC	689.5
	P r	666.5
	Pt disc	697.2
PSI		789.9
GRS*	Comb Pt	710
	UV	793
Statistics	**Average**	665
	SD	163
	RSD (%)	24.5
	Median	696

* For comparison purposes, only the results at the original ionic strength have been considered

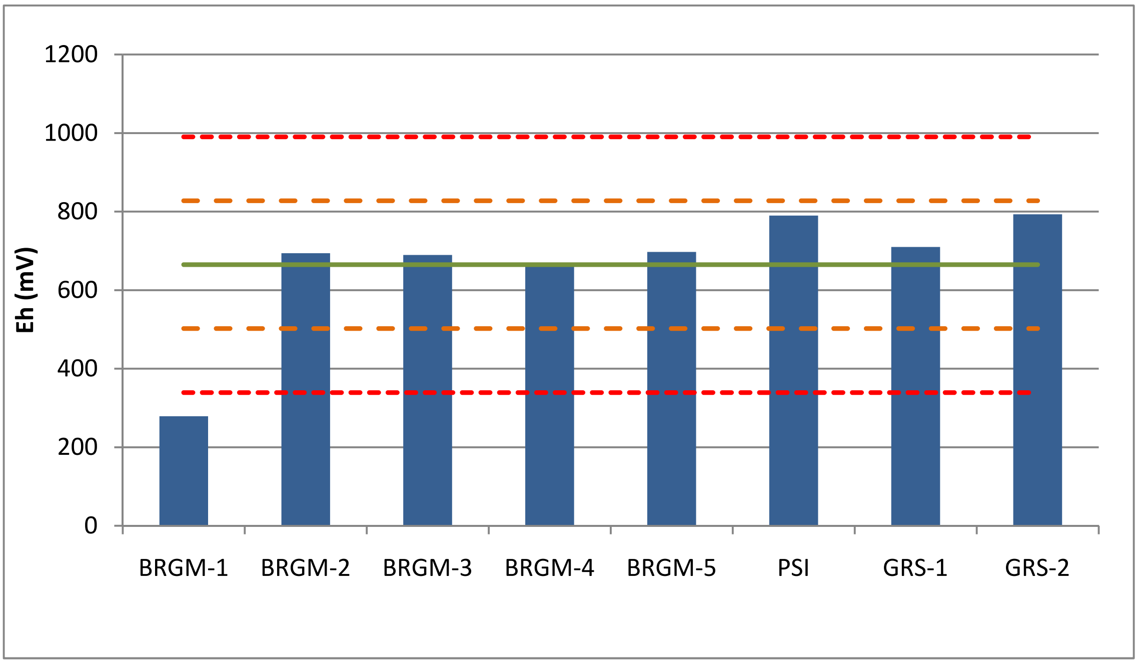


Figure 43.-Results obtained for sample REF 2 Ca c
Lines represent average value (green), ± SD (orange) and ± 2SD (red)

The box-plot (Figure 44) and frequency histogram (Figure 45) indicate that the BGRM measurement performed with the Pt electrode behaves as an outlier. After the removal of this anomalous value, the average value and standard deviation are + 720 ± 50 mV, with a relative standard deviation of 7%.

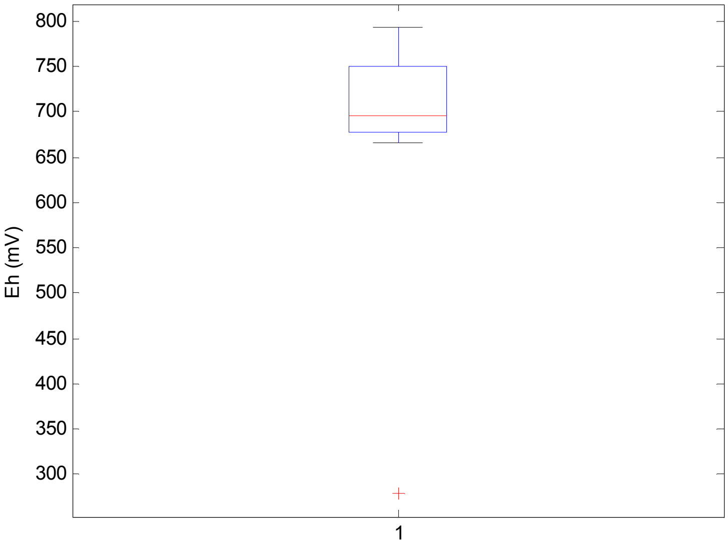


Figure 44.- Box-whisker plot of the results obtained for sample REF 2 Ca c

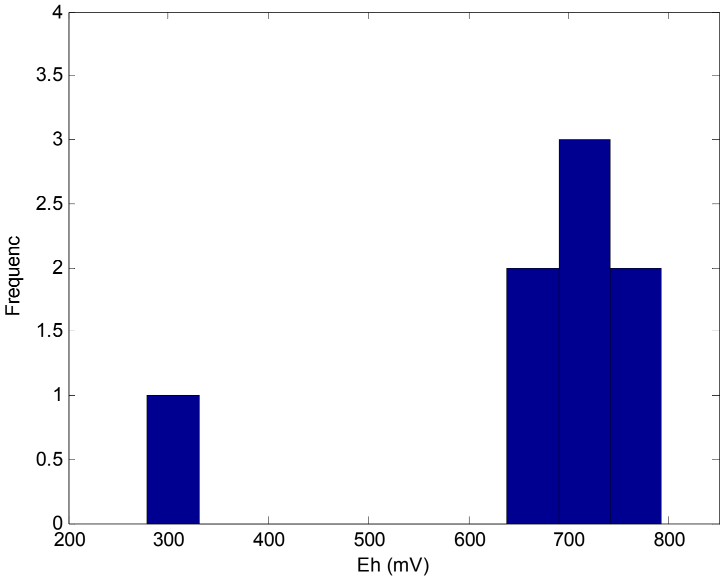


Figure 45.-Frequency histogram of the results obtained for sample REF 2 Ca c

3.3 Quinione systems (REF 3)

3.3.1 REF 3 HS a

Table 16 and Figure 46 show the replicate measurements for sample REF 3 HS a.

Table 16.- Summary of the results obtained for sample REF 3 HS a

Institution	Method/Replicate	Eh (mV)
CTH	1	307
	2	297
	3	320
FZD		285
ITU	Pt Static	319
	Pt Stirred	310
	Au Stirred	313
IPL	1	307.7
	2	320
PSI		185.4
CNRS	Amperometric: Pt UME glass	233
	Potentiometric: Pt RDE	206.3
Statistics	**Average**	284
	SD	47.6
	RSD (%)	16.8
	Median	307

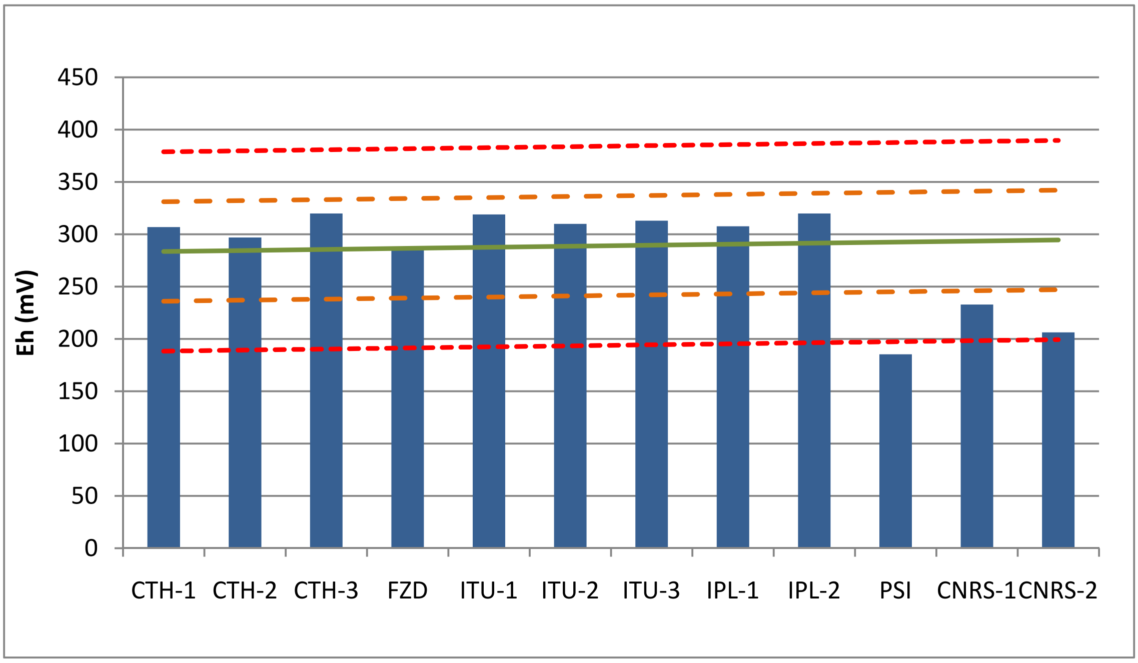


Figure 46.-Results obtained for sample REF 3 HS a
Lines represent average value (green), SD (orange) and 2SD (red)

The box-plot (Figure 47) indicates that the measurement from PSI behaves as an outlier. After removing this value from the results set, the average and standard deviation are +292 38 mV (RSD 13%).

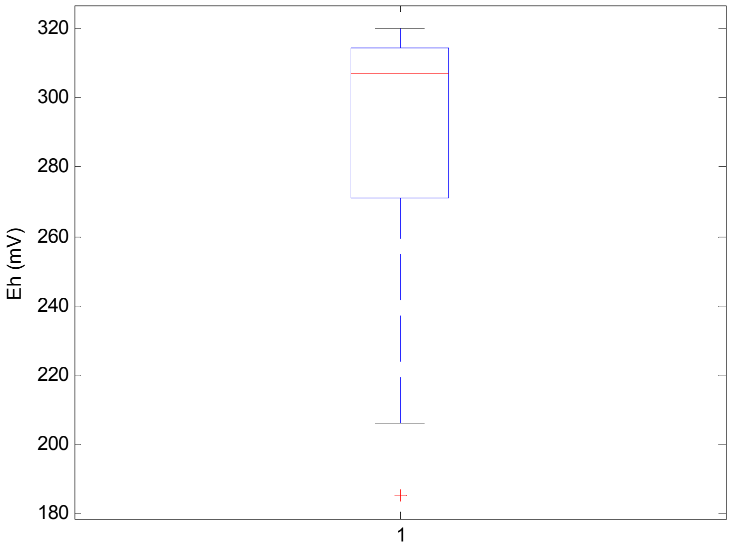


Figure 47.- Box-Whisker plot of the results obtained for sample REF 3 HS a

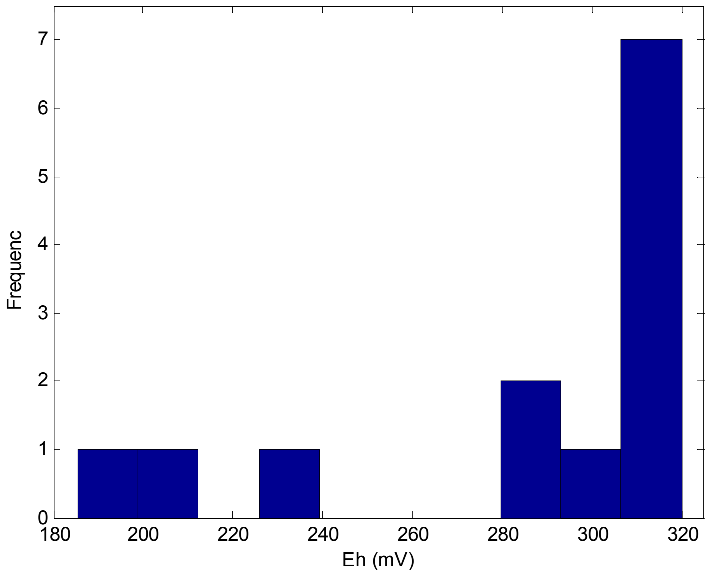


Figure 48.-Fequency histogram of the results obtained for sample REF 3 HS a

3.3.2 REF 3 ISe a

The replicate measurements of sample REF3 ISe a can be observed in Table 17 and Figure 49.

Table 17.- Summary of the results obtained for sample REF 3 ISe a

Institution	Method/Replicate	Eh (mV)
CTH	1	114
	2	146
	3	134
	4	124
FZD		165
ITU	Pt Static	142
	Pt Stirred	141
	Au Stirred	167
	Pt O Static	68
	Pt O Stirred	121
IPL	1	223.4
	2	179
PSI		136.8
CNRS	Amperometric: Pt UME glass	118
	Potentiometric: Pt RDE	139.6
Statistics	**Average**	141
	SD	34.7
	RSD (%)	24.6
	Median	140

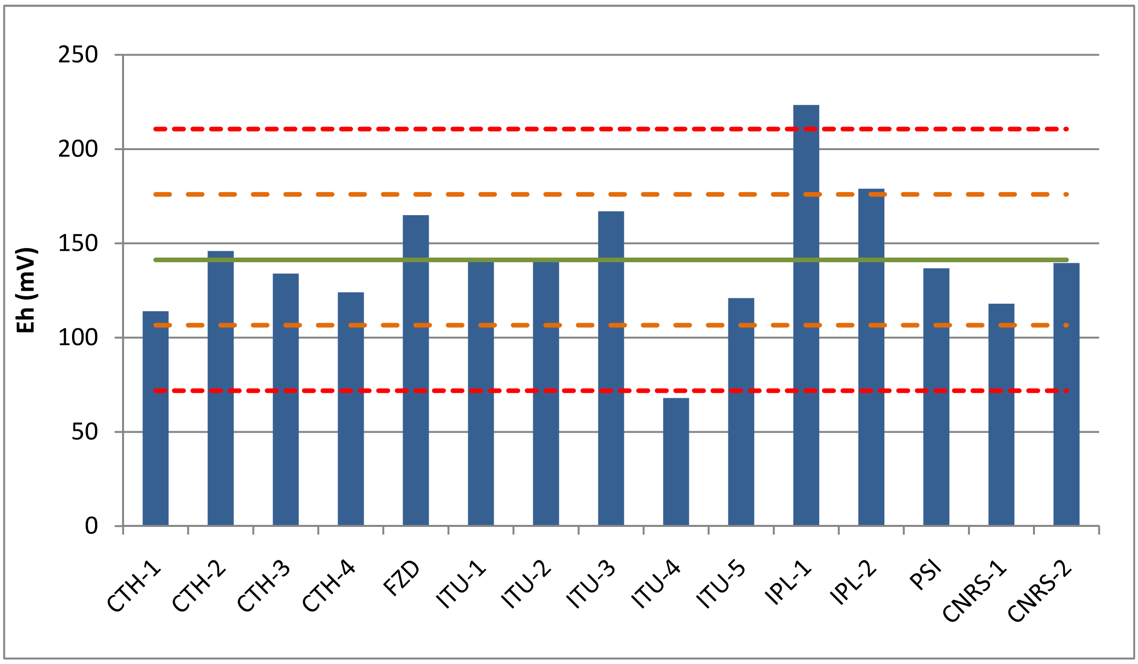


Figure 50.-Results obtained for sample REF 3 ISe a

Lines represent average value (green), SD (orange) and 2SD (red)

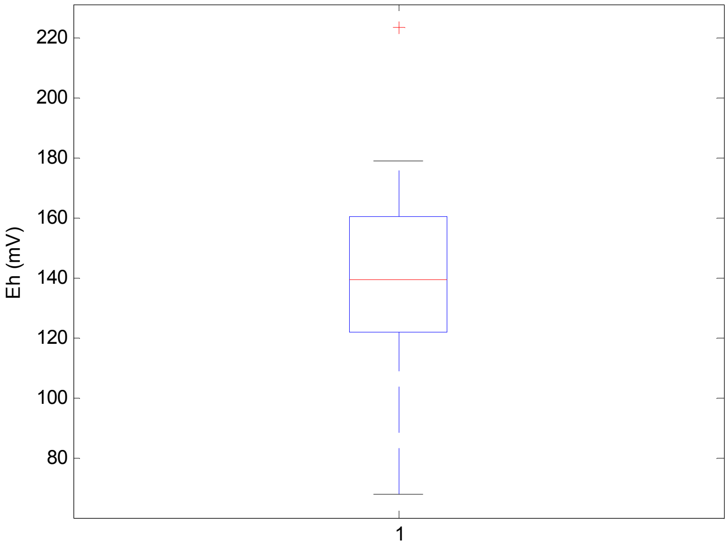


Figure 51.- Box-whisker plot of the results obtained for sample REF 3 ISe a

The frequency histogram shows that most of the results gather around an Eh value close to + 140 mV (Figure 52). The box-plot (Figure 52) of the replicates indicates that the 1st replicate of IPL behaves as an outlier. After removal of this value, the average and standard deviation are + 135 ± 27 (RSD 20%).

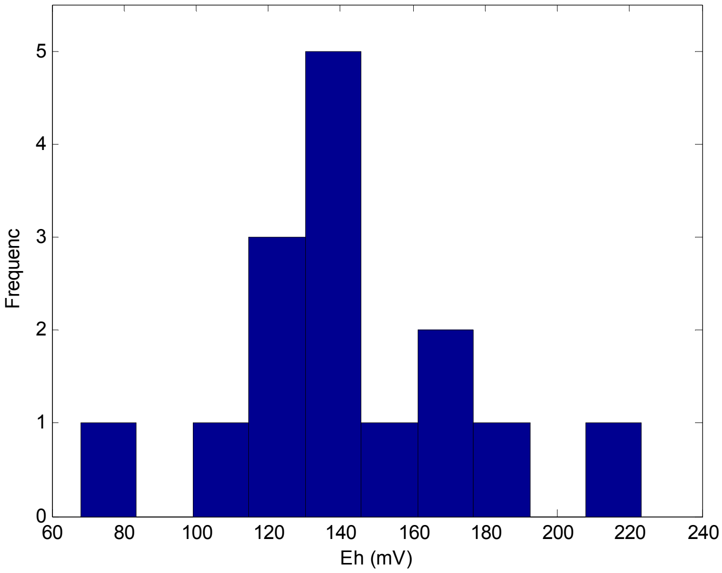


Figure 52.-Fequency histogram of the results obtained for sample REF 3 ISe a

3.3.3 REF 3 ISe b

Table 18 and Figure 52 summarise the results obtained for sample REF 3 ISe b. Four of the five replicate of sample REF ISE are negative values around -58 mV, whereas there is only on positive value of +10 mV. The box-plot (Figure 53) and frequency histogram (Figure 54) indicate that this value from FZD should be discarded. The new average value and standard deviation values are 59 6 mV (10% RSD).

Table 18.- Summary of the results obtained for sample REF 3 ISe b

Institution	**Method/Replicate**	**Eh (mV)**
FZD		10
PSI		-67
Amphos		-58
CNRS	Amperometric: Pt UME glass	-53
	Potentiometric: Pt RDE	-58.5
Statistics	**Average**	-45.3
	SD	31
	RSD (%)	69
	Median	-58

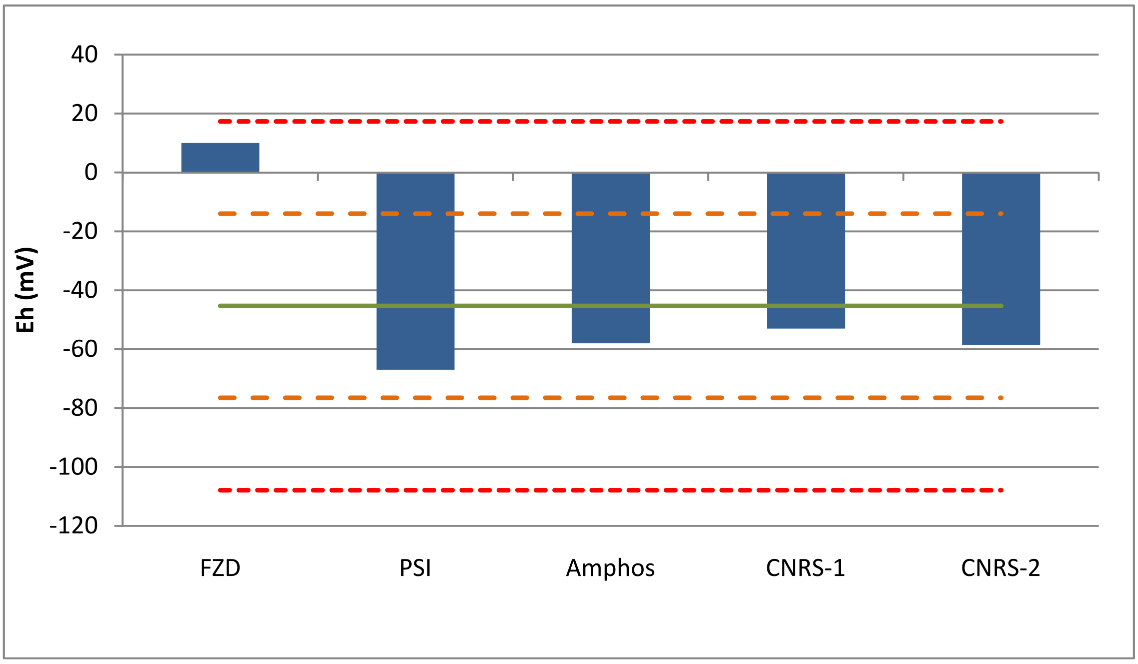


Figure 52.-Results obtained for sample REF 3 ISe b
Lines represent average value (green), SD (orange) and 2SD (red)

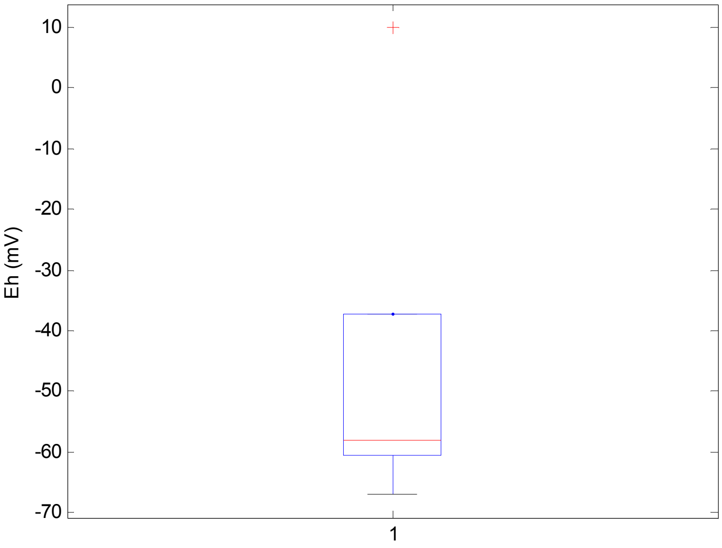


Figure 53.-Frequency histogram of the results obtained for sample REF 3 ISe b

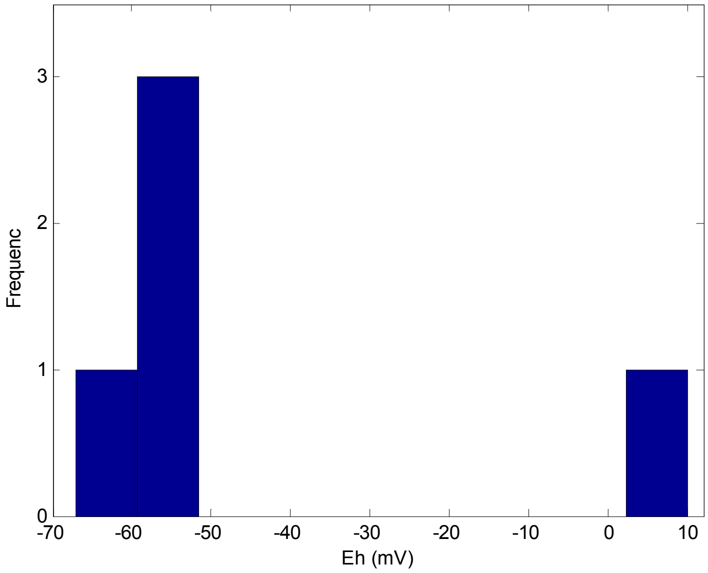


Figure 54.- Box-whisker plot of the results obtained for sample REF 3 ISe b

3.4 Hyperalkaline / Cement systems

3.4.1 REF 4 MQ1

Table 19 and Figure 55 summarise the results obtained for the sample REF 4 MQ1.

Table 19.- Summary of the results obtained for sample REF 4 MQ1

Institution	Method/Replicate	Eh (mV)
BRGM	Pt	-365
	Au	-548
	GC	-475
	P r	-422
	Pt disc	-511
PSI	Static	-474
	Stirred	-556
ULough		-597
Statistics	**Average**	-494
	SD	75.8
	RSD (%)	15.4
	Median	-493

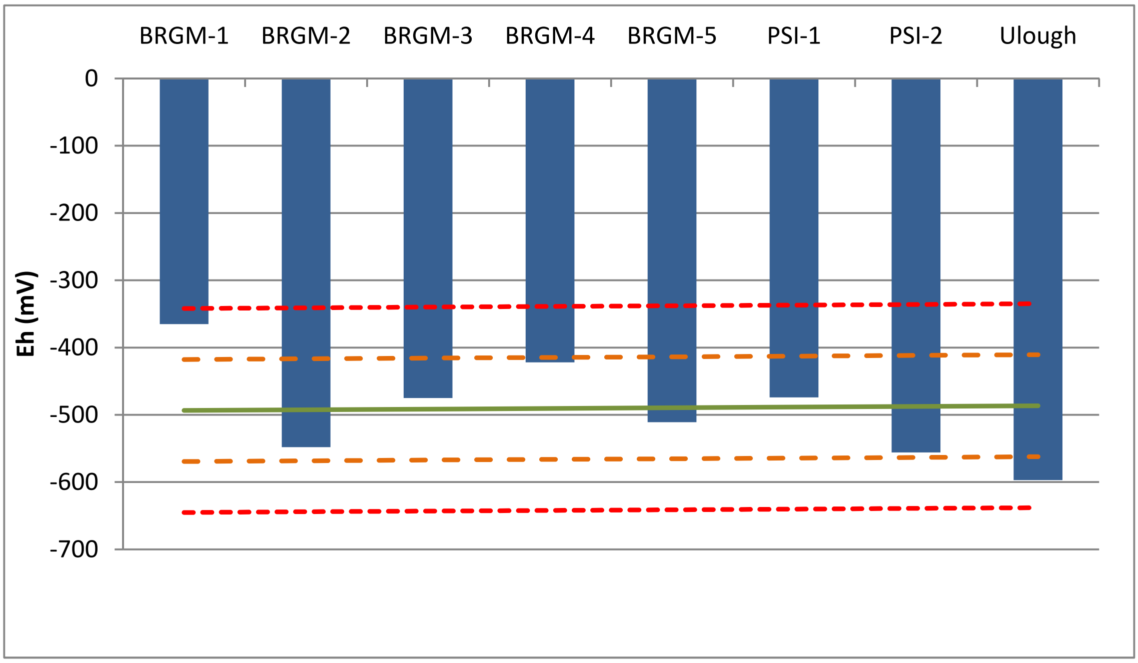


Figure 55.-Results obtained for sample REF 4 MQ1
Lines represent average value (green), SD (orange) and 2SD (red)

None of the results showed anomalous behaviour as can be concluded from the box-plot (Figure 58) and the frequency histogram (Figure 57).

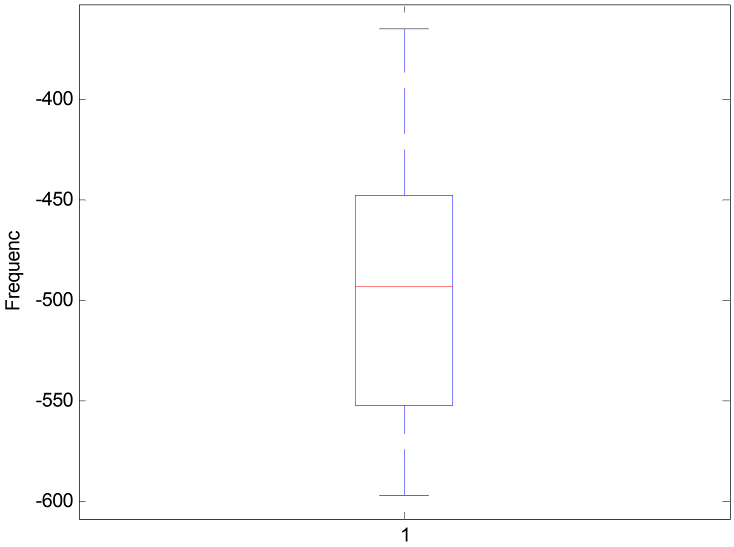


Figure 56.-Fequency histogram of the results obtained for sample REF 4 MQ1

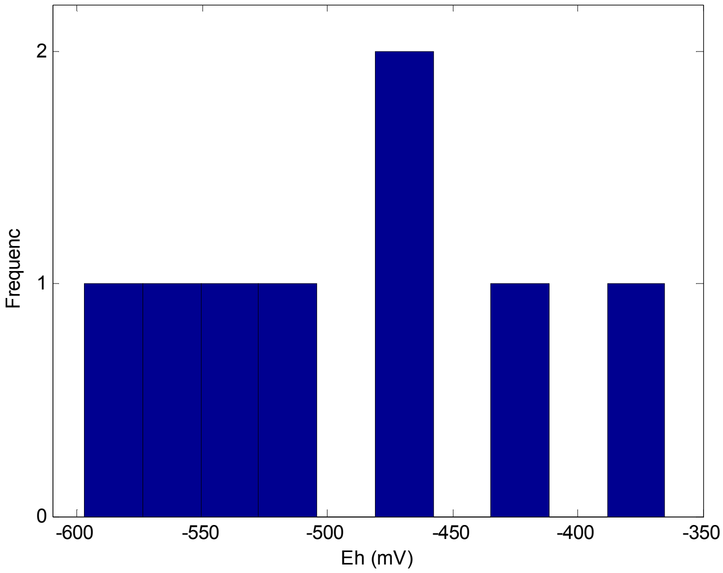


Figure 57.- Box - Whisker plot of the results obtained for sample REF 4 MQ1

3.4.2 REF 4 MQ2

Table 20 displays the replicate measurements for sample REF 4 MQ2, also represented in Figure 58.

Table 20.- Summary of the results obtained for sample REF 4 MQ2

Institution	Method/Replicate	Eh (mV)
BRGM	Pt	-434.4
	Au	-685.1
	GC	-575.6
	Pyr	-447.7
	Pt disc	-633.2
PSI	Static	-643
	Stirred 1	-725
	Stirred 2	-721.9
ULough		-663
Statistics	**Average**	-614
	SD	108
	RSD (%)	17.6
	Median	-643

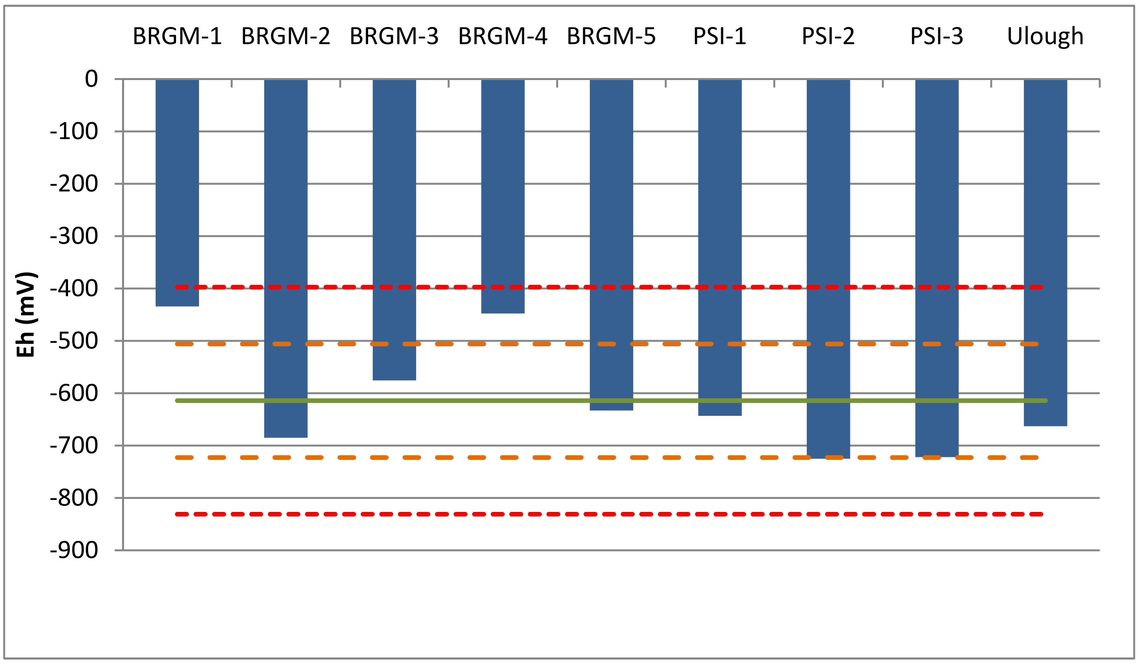


Figure 58.-Results obtained for sample REF 4 MQ2
Lines represent average value (green), ±SD (orange) and ±2SD (red)

As in the previous case (REF 4 MQ1), the first replicate from BGRM obtained with the Pt electrode showed slightly lower potentials (in absolute value) than the bulk of samples. However, due to the low number of replicates (n = 9) and their spread (Figure 60), this sample cannot be considered as an outlier (Figure 59).

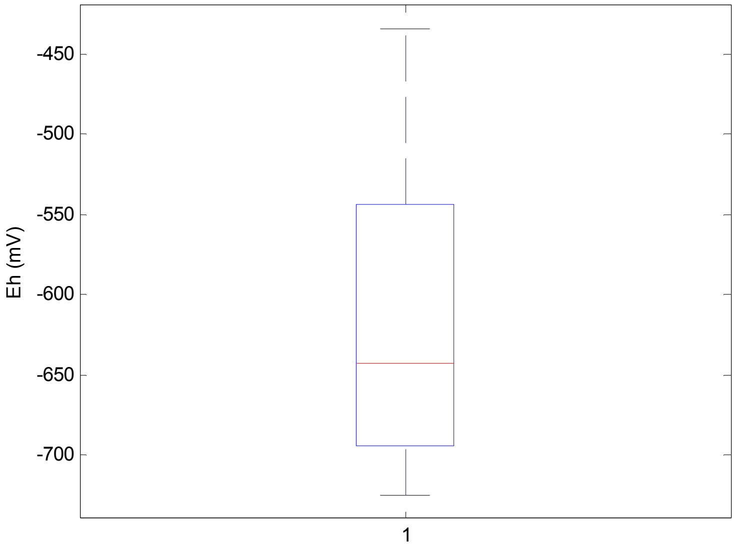


Figure 59.-Fequenc histogram of the results obtained for sample REF 4 MQ2

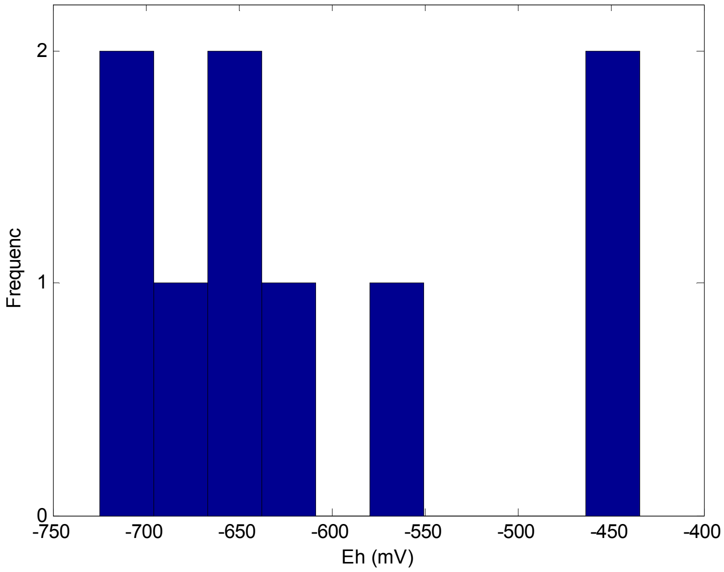


Figure 60.- Bo - hisker plot of the results obtained for sample REF 4 MQ2

3.4.3 REF 4 ACW1

Results obtained for sample REF 4 ACW1 are summarised in Table 21 and Figure 6**1.**

Table 21.- Summary of the results obtained for sample REF 4 ACW1

Institution	**Method/Replicate**	**Eh (mV)**
BRGM	Pt	-350.9
	Au	-707.5
	GC	-688.3
	P r	-567.9
	Pt disc	-723.3
Amphos		-755
IPL	1	-712
	2	-705
PSI	Static	-663
	Stirred 1	-738.2
	Stirred 2	-766.6
ULough		-614
Statistics	**Average**	-666
	SD	114
	RSD (%)	17.2
	Median	-706

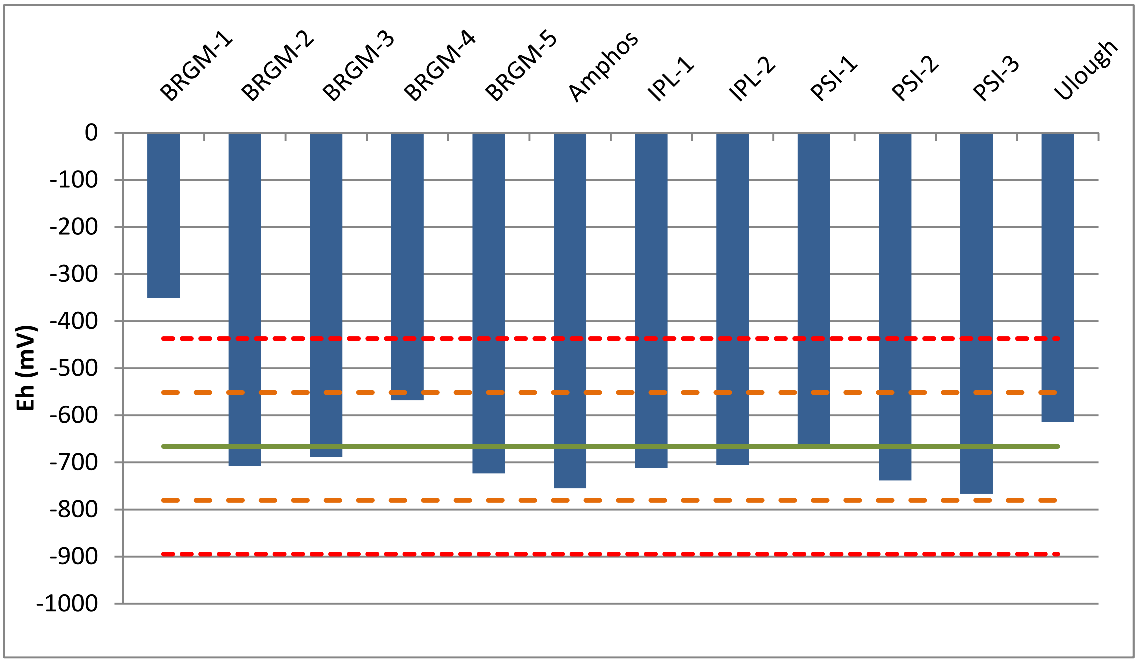


Figure 61.-Results obtained for sample REF 4 ACW1
Lines represent average value (green), ± SD (orange) and ± 2SD (red)

For this sample, the BGRM measurement performed with the Pt electrode, is clearly separate from the rest of the set of results (Figure 62 and 63), therefore, it can be considered as an outlier. After removal of this value, the average and standard variation values are -695 ± 60 mV (9% RSD).

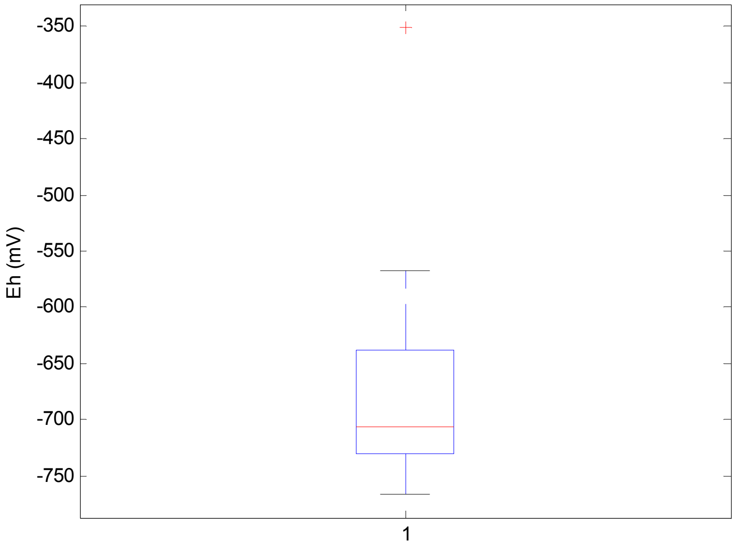


Figure 62.-Fequency histogram of the results obtained for sample REF 4 ACW1

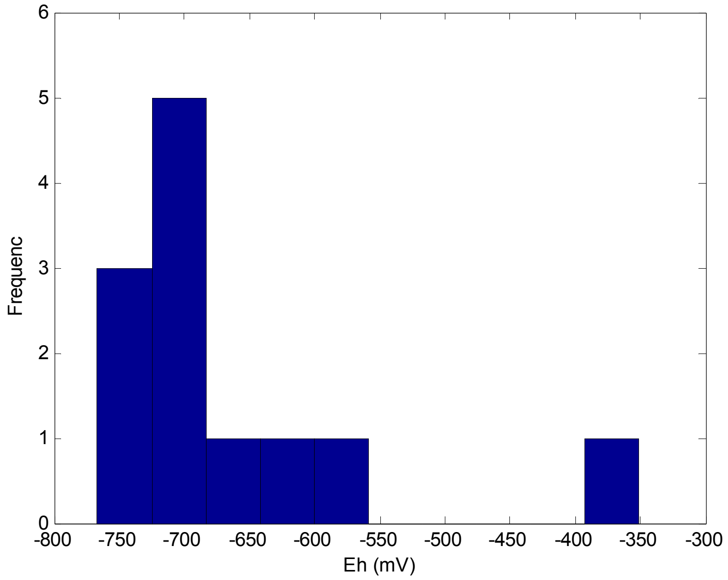


Figure 63.- Box-whisker plot of the results obtained for sample REF 4 ACW1

3.4.4 REF 4 ACW2

Table 22 summarises the results obtained for sample REF 4 ACW2, represented in Figure 64.

Table 22.- Summary of the results obtained for sample REF 4 ACW2

Institution	**Method/Replicate**	**Eh (mV)**
BRGM	Pt	-458
	Au	-737
	GC	-665
	Pyr	-443
	Pt disc	-700
Amphos		-775
IPL	1	-766
	2	-780
PSI	Static	-706
	Stirred 1	-754
	Stirred 2	-786.2
ULough		-606
Statistics	**Average**	-681
	SD	120
	RSD (%)	17.6
	Median	-722

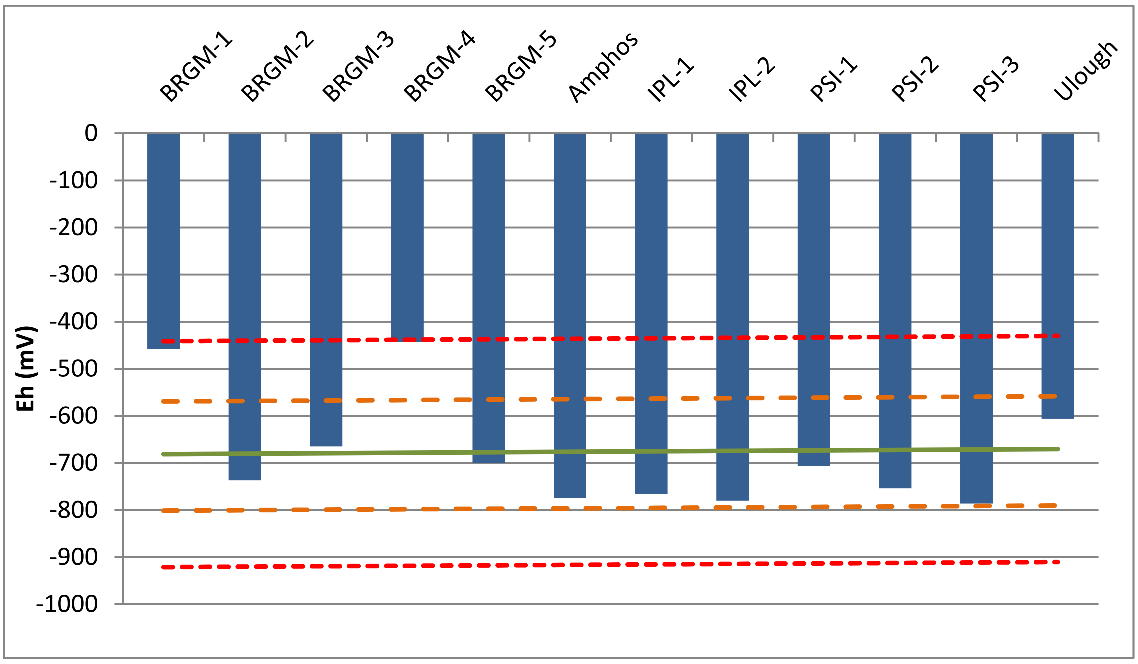


Figure 64.-Results obtained for sample REF 4 ACW2
Lines represent average value (green), ±SD (orange) and ±2SD (red)

The box-plot (Figure 65) does not point to any of the replicates as an outlier, although the frequency histogram (Figure 66) shows how the 1st replicate from BGRM separates from the remaining set of results. The most frequent result would correspond to an Eh value around -780 mV (Figure 66).

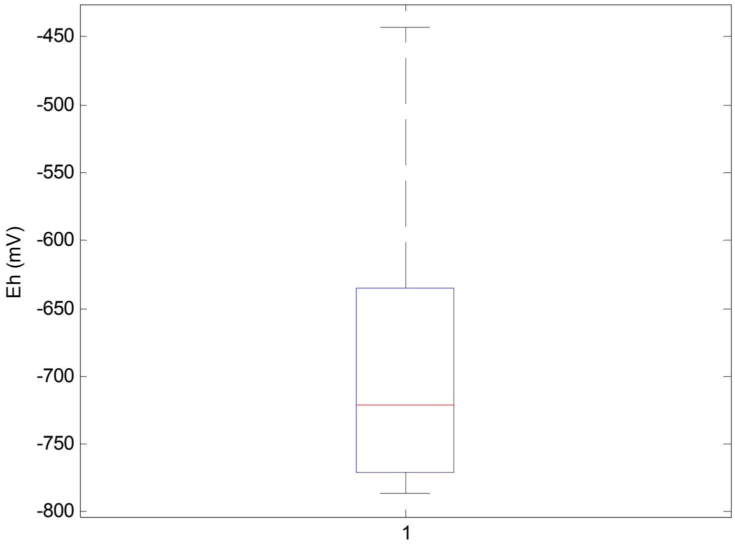


Figure 65.- Bo - hisker plot of the results obtained for sample REF 4 ACW2

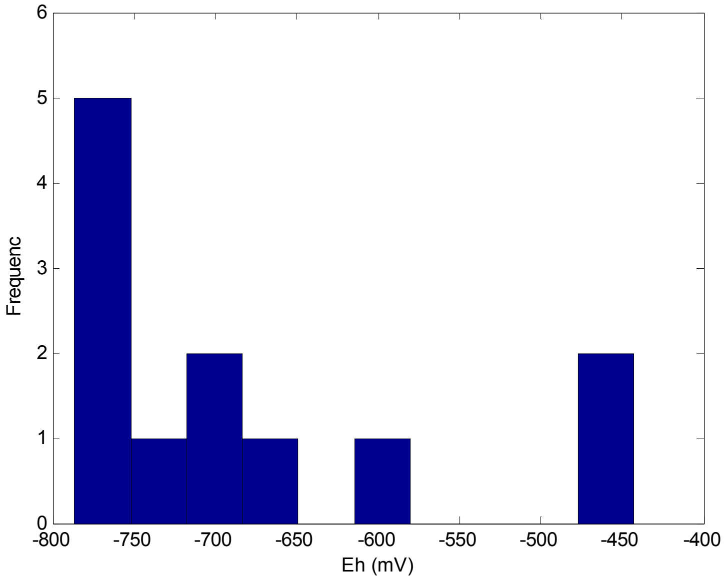


Figure 66.-Fequenc histogram of the results obtained for sample REF 4 ACW2

3.5 (Near)-Natural ground and porewater (NAT)

3.5.1 NAT 1a

Table 23 and Figure 67 summarise the results for sample NAT 1a.

Table 23.- Summary of the results obtained for sample NAT 1a

Institution	Method/Replicate	Eh (mV)
Amphos	1	27
	2	54
CTH	1	-77
	2	-106
	3	-122
FDZ		193
INE	Single Pt	164.3
	Single Au	134.9
	Single GC	177.8
	Comb Pt	242.1
	Single Pt	195.8
IPL	1	343.7
	2	330
MSU-INE	Prot 1	388
	Prot 2	298
	Prot 3	345
	Prot 4	301
PSI	Suspension	186.9
	Supernatant	182.8
ULough		185
Statistics	**Average**	172
	SD	151
	RSD (%)	88
	Median	186

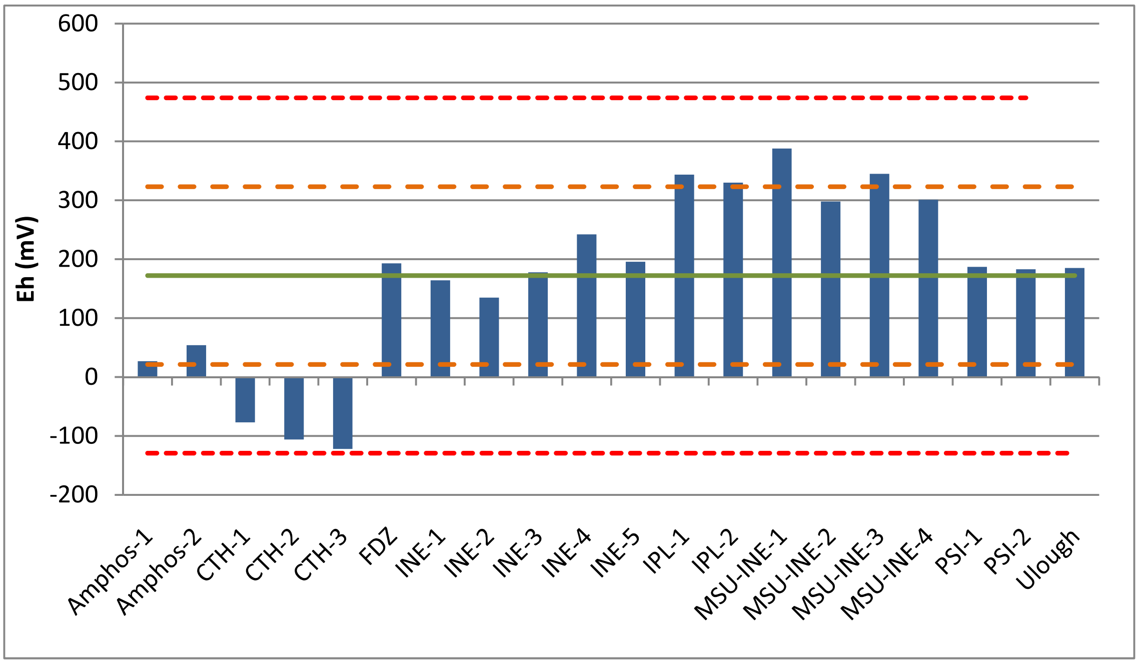


Figure 67.-Results obtained for sample NAT 1a
Lines represent average value (green), SD (orange) and 2SD (red)

As it can be seen in Figure 67, the three replicate measurements from CTH show a distinctive behaviour, being the only ones that provide negative Eh values. The main set of results gathers around +200 and +300 mV (Figure 69). The results are spread over a wide range and do not follow a normal distribution, as it can be observed from the frequency histogram. However, none of the samples could be considered as an outlier, because of the big scattering of the results (Figure 68), which show a relative standard deviation of 88%.

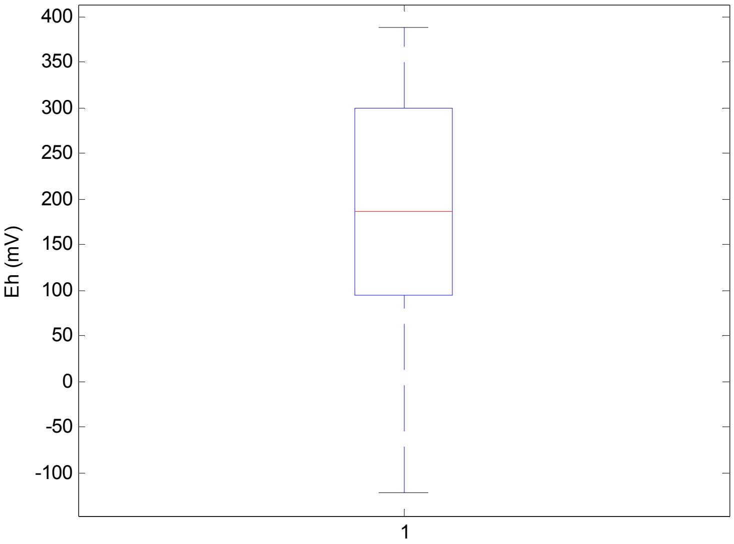


Figure 68.- Box-whisker plot of the results obtained for sample NAT 1a

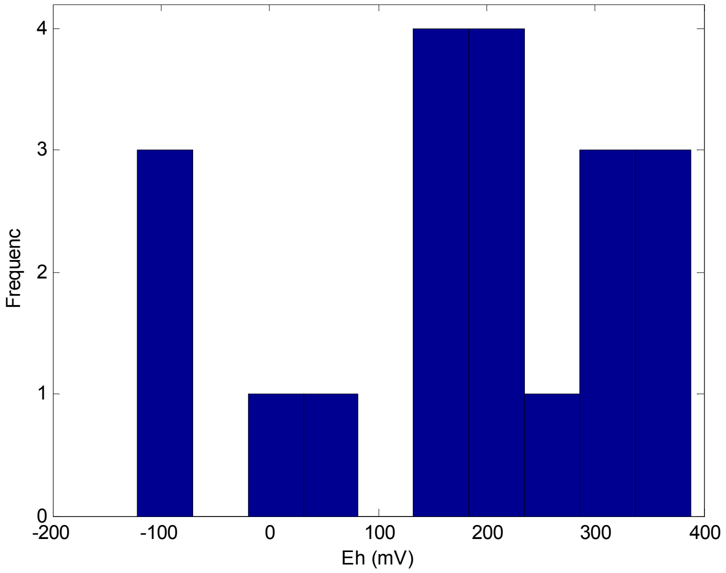


Figure 69.-Frequency histogram of the results obtained for sample NAT 1a

4.5.2 NAT 1b

Table 24 and Figure 70 collect the results obtained for sample NAT 1b.

Table 24.- Summary of the results obtained for sample NAT 1b

Institution	Method/Replicate	Eh (mV)
Amphos		82
FDZ		336
GRS	Comb Pt	328.96
	UV	419.84
INE	Single Pt	417
	Single Au	357.1
	Single GC	384.8
	Comb Pt	325.4
	Single Pt	559.7
PSI	Suspension, stirred	154.6
	Supernatant	230.5
ULough		171
Statistics	**Average**	314
	SD	134
	RSD (%)	43
	Median	332

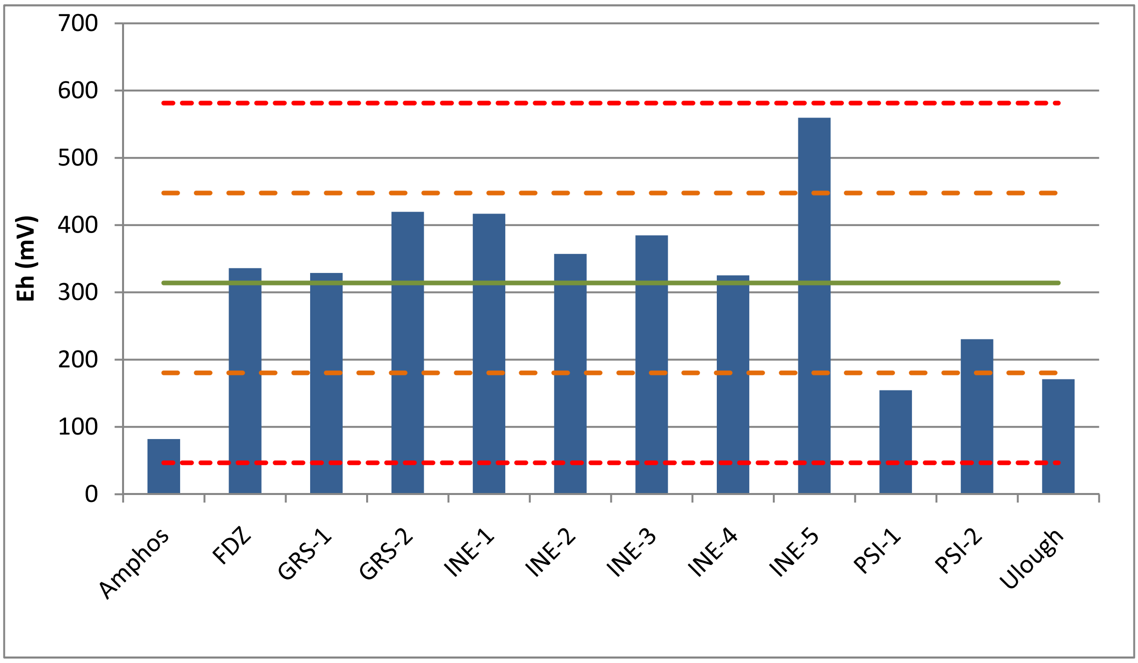


Figure 70.-Results obtained for sample NAT 1b
Lines represent average value (green), SD (orange) and 2SD (red)

Despite the big scattering of results (43% RSD), none of the samples could be classified as an outlier (Figures 71 and 72). The most frequent Eh value is around + 350 mV

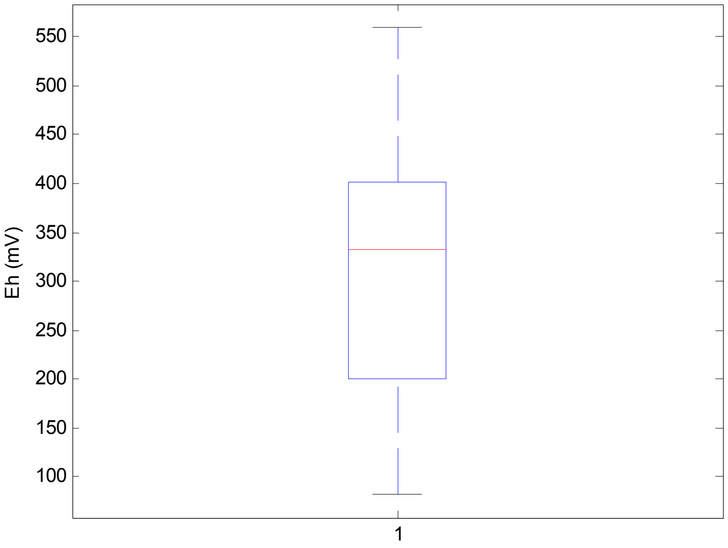


Figure 71.- Box - whisker plot of the results obtained for sample NAT 1b

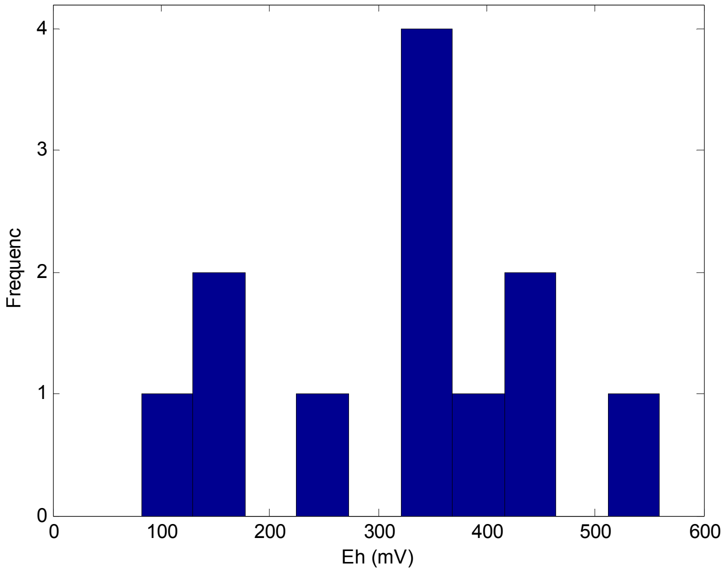


Figure 72.-Fequency histogram of the results obtained for sample NAT 1b

3.5.3 NAT 2

Table 25 and Figure 73 show the replicate measurements for sample NAT 2.

Table 25.- Summary of the results obtained for sample NAT 2

Institution	Method/Replicate	Eh (mV)
Amphos	1	95
	2	54
FDZ		279
CTH	1	322
	2	322
	3	393
INE	Comb Pt	275
IPL	1	384.1
	2	310
PSI	Suspension, stirred	249.2
ULough		87
CNRS	Amperometric: Pt UME glass	-398
	Amperometric: Pt UME glass	127
	Potentiometric: Pt RDE	-186.6
	Potentiometric: Pt RDE	97.1
	Potentiometric: Pt wire	317.6
	Potentiometric: Pt wire	-34.7
	Potentiometric: Pt wire	278.3
Statistics	**Average**	165
	SD	210
	RSD (%)	127
	Median	262

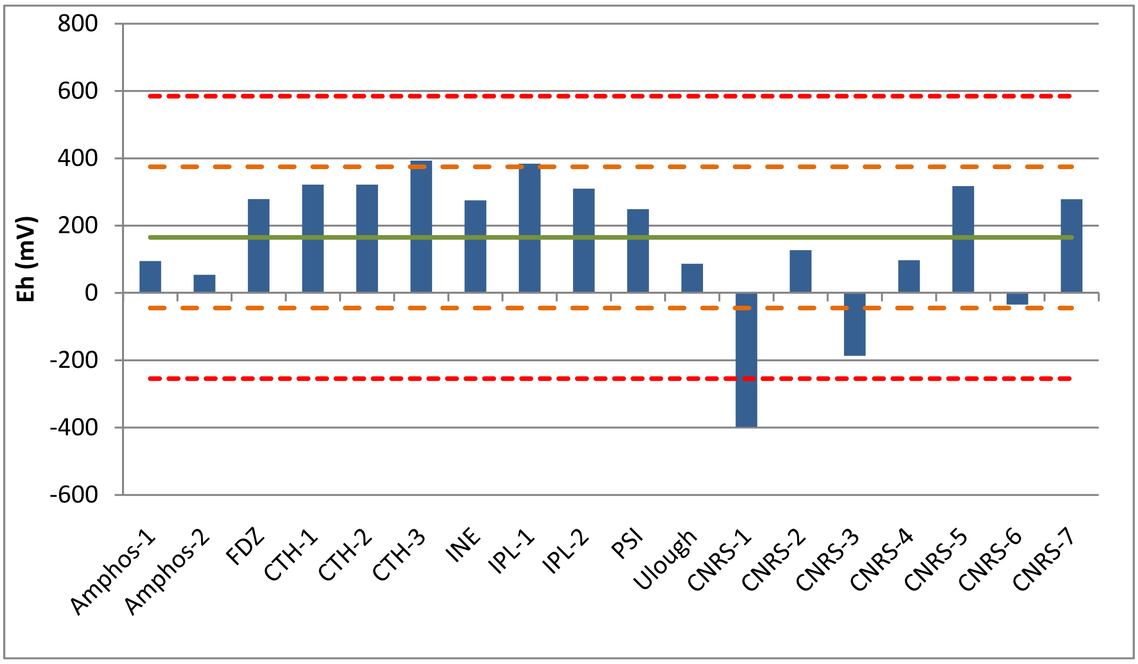


Figure 73.-Results obtained for sample NAT 2
Lines represent average value (green), ±SD (orange) and ±2SD (red)

The box-plot of the results (Figure 74) classifies the 1st amperometric measurement from CNRS as an outlier. After the removal of this replicate, the remaining set of results shows still a big scattering, with average and standard deviation values of + 198 ± 160 mV (81% RSD). The frequency histogram shows that the most frequently obtained values gather around +350 mV (Figure 75).

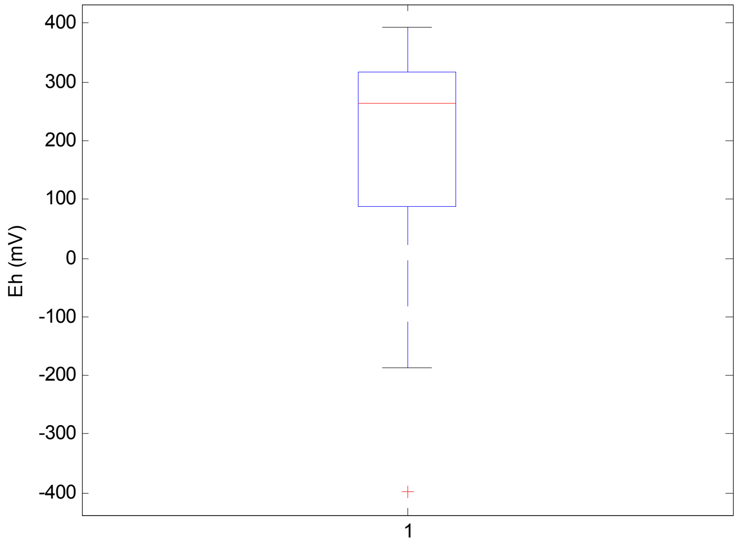


Figure 74.- Box-whisker plot of the results obtained for sample NAT 2

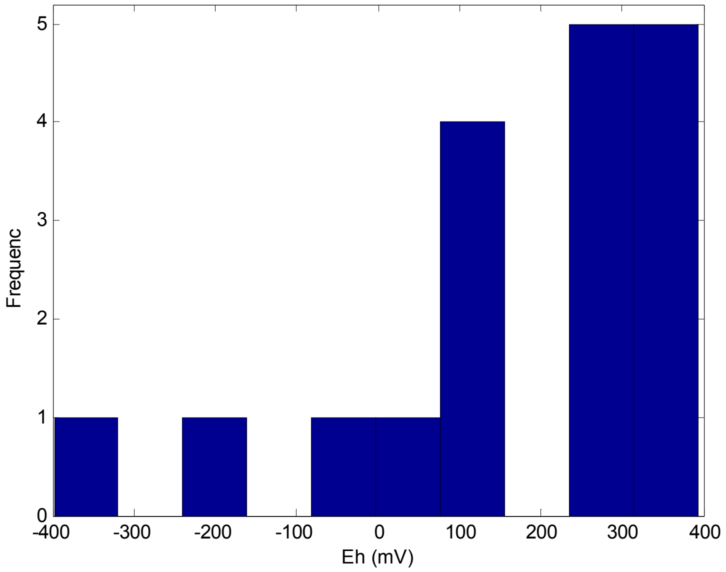


Figure 75.-Fequency histogram of the results obtained for sample NAT 2

3.5.4 NAT 3

Table 26 and Figure 76 show the results obtained for sample NAT 3.

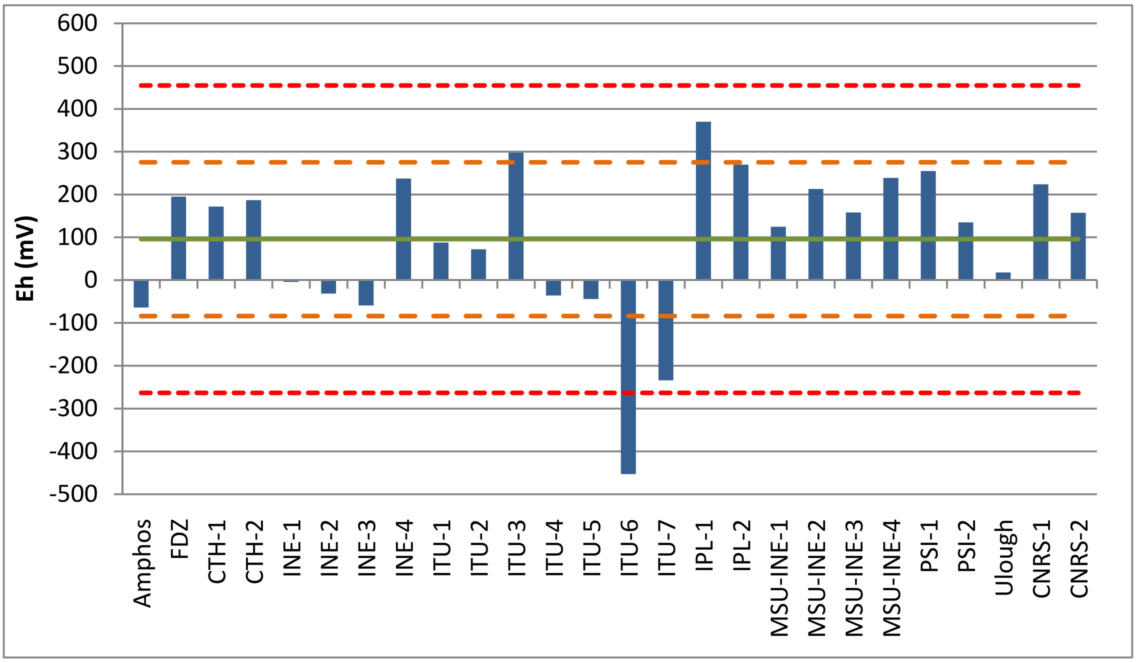


Figure 76.-Results obtained for sample NAT 3
Lines represent average value (green), SD (orange) and 2SD (red)

Table 26.- Summary of the results obtained for sample NAT 3

Institution	**Method/Replicate**	**Eh (mV)**
Amphos		-64
FDZ		195
CTH	1	172
	2	187
INE	Single Pt	-4.2
	Single Au	-31.4
	Single GC	-59.1
	Single Pt	237.2
ITU	Pt Static	88
	Pt Stirred	72
	Comb Au stirred	298
	RHE Pt O Static	-36
	RHE Pt O Stirred	-44
	RHE Pt O reference removed, static	-453
	RHE Pt O reference removed, stirred	-234
IPL	1	370
	2	270
MSU-INE	Prot 1	125
	Prot 2	213
	Prot 3	158
	Prot 4	239
PSI	Suspension 1	255
	Suspension 2	135
ULough		18
CNRS	Amperometric: Pt UME glass	224
	Potentiometric: Pt RDE	157.5
Statistics	**Average**	96
	SD	180
	RSD (%)	188
	Median	146

Replicates range in a wide interval of Eh value, from -453 mV to + 370 mV, with a massive relative standard deviation of 188%. The box-plot of results (Figure 77) indicates that the 6th replicate from ITU) under static condition and reference electrode outside the sample during the stabilisation time) should be treated as an outlier. After removal of this value, the recalculated average and standard deviation values are +118 ± 143 mV (note that the SD value is larger than the average value itself, 122% RSD). The frequency histogram (Figure 78) shows that the most frequently obtained value ranged between +150 and +250 mV.

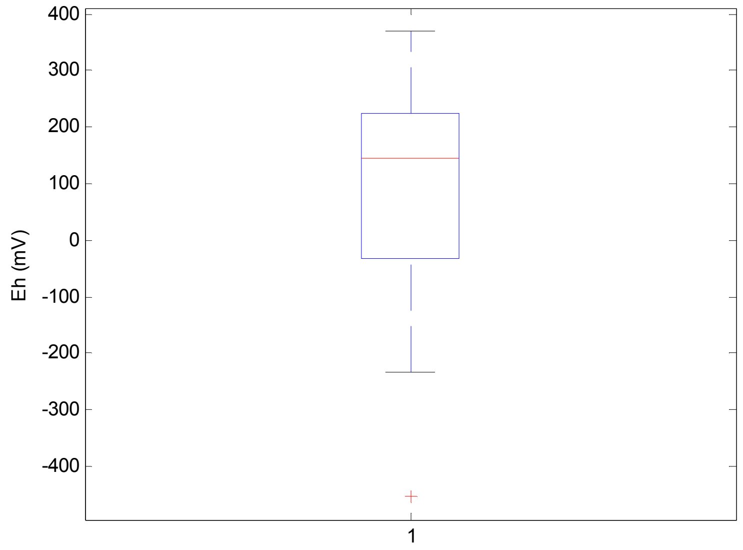


Figure 77.- Box-whisker plot of the results obtained for sample NAT 3

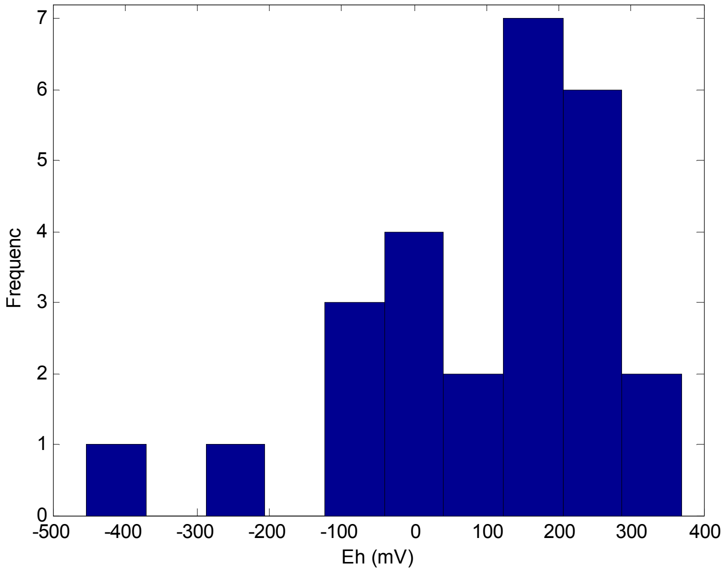


Figure 78.- Frequency histogram of the results obtained for sample NAT 3

3.5.5 NAT 4

Table 27 summarises the results obtained for sample NAT4, represented in Figure 79.

Table 27.- Summary of the results obtained for sample NAT 4

Institution	Method/Replicate	Eh (mV)
Amphos		666
FDZ		674
GRS*	Comb Pt	685.6
	UV	672.9
INE	Comb Pt	648
MSU-INE	Prot 1	654
	Prot 2	661
	Prot 3	654
	Prot 4	665
PSI		575
ULough		487
Statistics	**Average**	640
	SD	58
	RSD (%)	9.1
	Median	661

* For comparison purposes, only the results at the original ionic strength have been considered

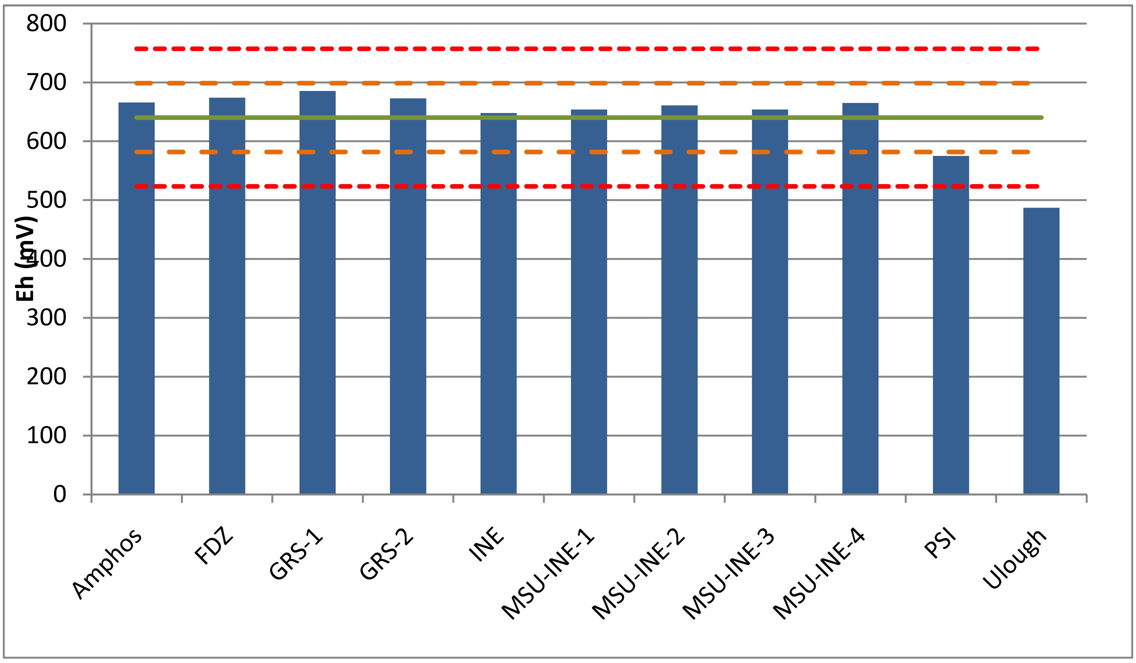


Figure 79.-Results obtained for sample NAT 4
Lines represent average value (green), SD (orange) and 2SD (red)

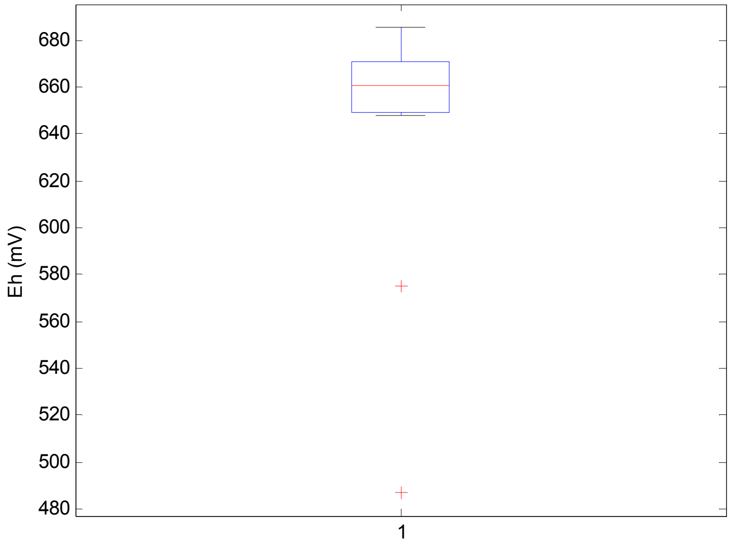


Figure 80.- Box-whisker plot of the results obtained for sample NAT 4

Both replicates from PSI and Loughborough University, produced values below the average, and are classified by the box-plot (Figure 80) as outliers. After the removal of these values, the average and standard deviation are + 664 ± 12 mV (1.8% RSD).

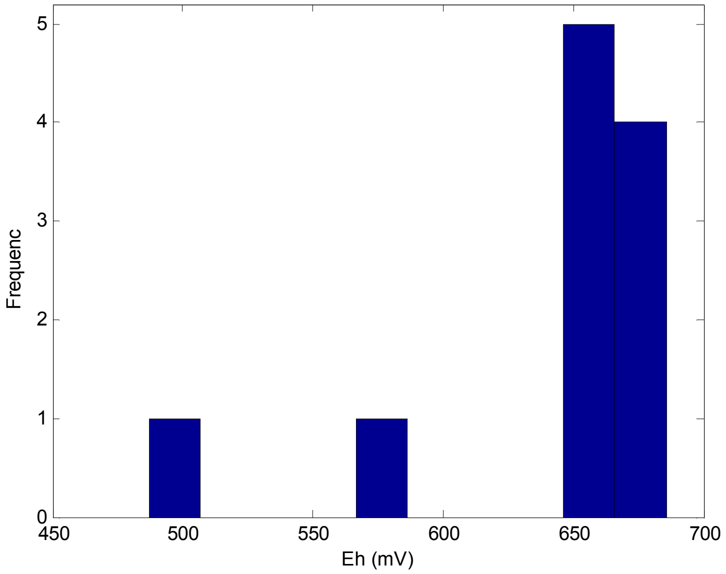


Figure 81.- Frequency histogram of the results obtained for sample NAT 4

3.6 Microbial systems (MIC)

3.6.1 MIC A1

Table 28 and Figure 82 summarise the results obtained for sample MIC A1.

Table 28.- Summary of the results obtained for sample MIC A1

Institution	**Method/Replicate**	**Eh (mV)**
FZD		-135
MSU-INE	Prot 1	-314
	Prot 2	-317
	Prot 3	-315
	Prot 4	-311
PSI	Stirred	-266.4
Statistics	**Average**	-276
	SD	72
	RSD (%)	26
	Median	-312

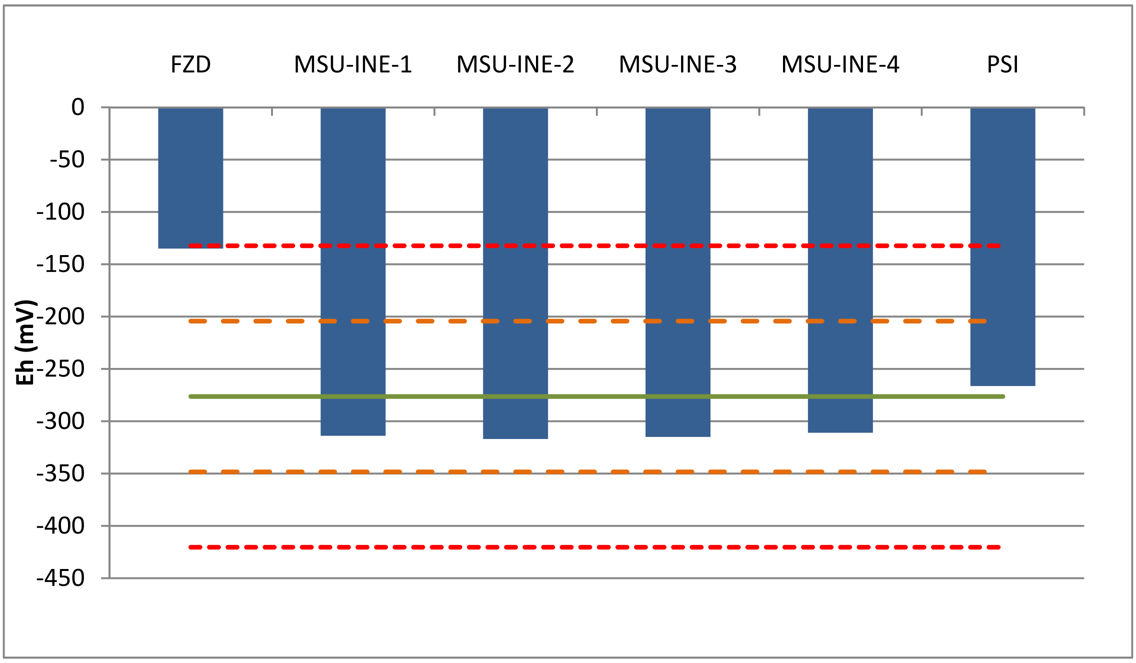


Figure 82.-Results obtained for sample MIC A1
Lines represent average value (green), ±SD (orange) and ±2SD (red)

The replicate from FDZ behaves as an outlier (Figure 83). After removal of this replicate the average and standard deviation values are -305 ± 22 mV (7% RSD).

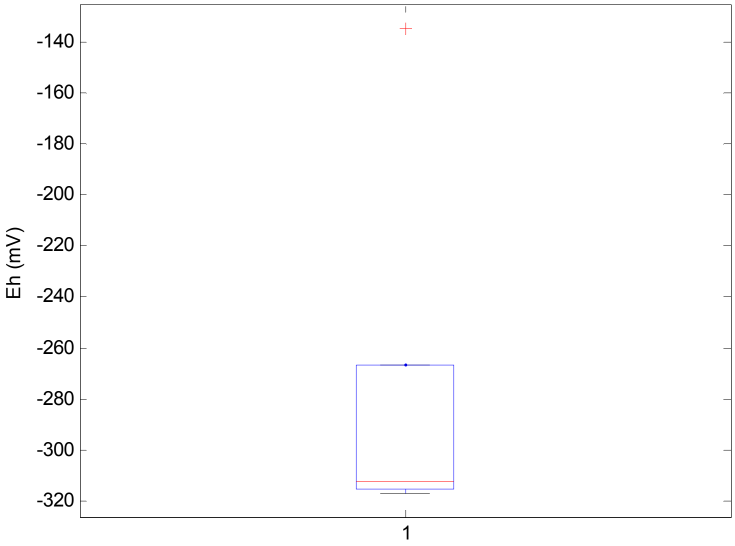


Figure 83.- Bo - hisker plot of the results obtained for sample MIC A1

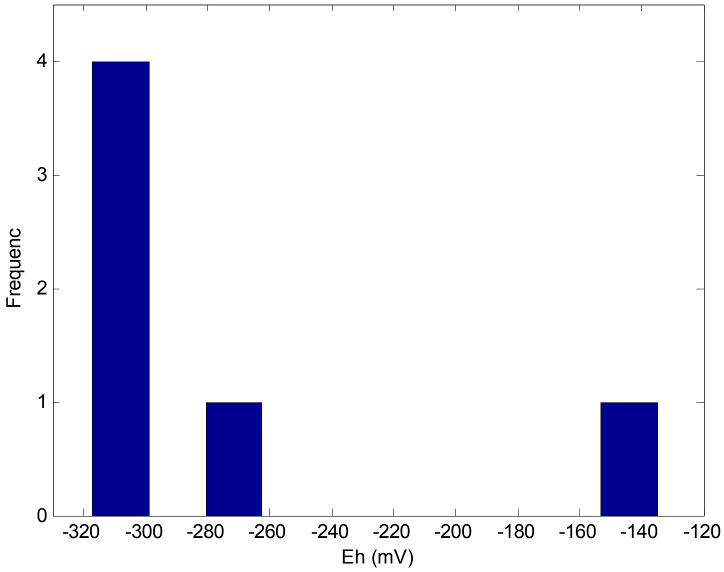


Figure 84.-Fequenc histogram of the results obtained for sample MIC A1

5. General conclusions

In general terms, Eh measurement produces a very large amount of scatter, with relative standard deviation values that range from 10% to up to ca. 350%, regardless the nature of the sample. However, it must be noted that the four samples representing hyperalkaline/cement systems had quite consistent deviations (around 16-18% RSD) with Eh values from -400 to -700 mV.

In suspensions, the measurement of the Eh in the whole suspension differs significantly from the measurements of Eh in the supernatant and filtrate. This should be taken into consideration, and the relative suitability of each of the types of measurements would depend on the particular objectives of the study. Although stirring could have an effect on stabilisation time, it did not have significant effect on the final values and results could not be differentiated according to this factor.

ReCosy, Intercomparison Exercise

Within Workpackage 2 “Development of redox determination methods”

UPPC (15):

Fiber-optical sensing of oxygen in reference and natural samples

Dörte Steinbrück and Michael U. Kumke

Background and objectives

In reference and natural samples the oxygen concentrations were measured based on fiber-optical sensing. Here, the tip of a tapered optical fiber was coated with an oxygen permeable polymer, in which a luminescent dye is embedded. The luminescence of the latter is quenched by oxygen. The degree of luminescence quenching is related to the oxygen concentration. The luminescence quenching can be detected either as a decrease in luminescence intensity or as a decrease of the decay time. In the present work, a phase-modulation detection technique is applied to determine the luminescence decay time of the probe.

Compared to standard (fiber-)optical detection schemes, the measurements can be carried out under room light and in the presence of other “background” luminescence. The latter is of great importance since in natural samples the presence of intrinsic luminescence due to e.g. natural organic matter (such as humic substances, chlorophyll etc.) can complicate luminescence measurements. Using a dual-phase modulation approach, unwanted contributions from background components can be eliminated. Optical-based oxygen measurements at concentration levels > 1% O_2 can be considered as well-established (e.g., applications in life science). However, at trace level concentrations less or no data are available.

The dual-frequency phase modulation technique was implemented for O_2 determination in different types of biological samples such as plant cells. Although challenging, the matrices investigated so far differ greatly from the ones to be tested during the ICE with respect to the possible interferences (e.g., poisoning of polymer, cross sensitivity). For measurements in different media, sensitivity and the dynamic response of the particular sensor (especially the polymer matrix) to matrix components such as humic substances has to be evaluated. Especially for the prototype sensor (type II) general parameters for measurements at very low oxygen concentrations need to be determined. Important settings to be optimized are the modulation frequencies for luminescence measurements at very low concentrations since the observed magnitude of the phase shifts is strongly interconnected and subsequently also the precession of the determined oxygen concentration. Another important issue is a proper calibration of the prototype sensor for determination of very low oxygen concentrations, since reliable standards are difficult to obtain.

During the ICE two different sensors, based on different luminescence dyes, were tested in different reference and natural samples in order to

i) test the stability of optical sensors in different matrices (“poisoning of the sensor, especially the polymer matrix, cross sensitivities, suppression of background arising from the matrix)
ii) the sensitivity of the different sensors for oxygen at trace level concentration
iii) comparison with electrochemical methods
iv) (testing and comparing different luminescence probes with respect to i) – iii))

Experimental method and approach

Since a direct fiber-optical coupling of the detector into a glove box was not possible, the samples were kept under an Argon atmosphere all time and measurements were performed outside of the glove box. About five millilitres of each sample were transferred to sealed glass containers. The optical fiber was directly injected into the sample and the luminescence signal was recorded. In the measurements different in-lab built fiber-sensors (tapering and coating with polymer and dye mixture) were used. For calibration, measurements at 0%, 3 *vol*% and 20.9 *vol*% O_2 concentration were performed. In addition, a sample with 100 ppm O_2 was used as an additional reference.

In between two sample measurements the calibration was checked in order to monitor alterations of the sensor due to "poisoning" from matrix components.

Two sets of fiber-sensors were tested

i) Type I: standard sensor set up (with luminescence decay time τ_0 = 65 µs)
ii) Type II: a prototype sensor (with τ_0 = 650 µs)

Samples measured

The following samples sets were measured:

- Homogeneous systems with microbiological activity: MIC A1, MIC A2, MIC B1, and MIC B2
- Groundwater with humic substances (Gorleben): NAT 1a, NAT 1b
- Clay-rock system (COX): NAT 2
- Granitic ground water (Grimsel): NAT 3

Outcome of the study

In summary, the ICE initiated the integration and improvement of technical components in the fiber-optical set up, which led to the implementation of a novel sensor (type II) for oxygen measurements at very low concentrations.

i) Oxygen measurements carried out using sensors of type I

The sensor showed a very stable performance in all matrices investigated. The determined oxygen concentrations for all samples investigated were very low, which was expected based on the preparation history of the samples. The standard sensor of type I was tested in the samples with respect to possible matrix effects by bubbling of oxygen (of different concentration: 3 *vol*% and 20.9 *vol*%). Compared to the corresponding calibration in clear water, no significant "aging" was observed.

Sample	MIC A1	MIC A2	MIC B1	MIC B2	NAT 1a	NAT 1b	NAT 2	NAT 3
O2 / ppm[1]	472	0	462	286	0	164	200	2417

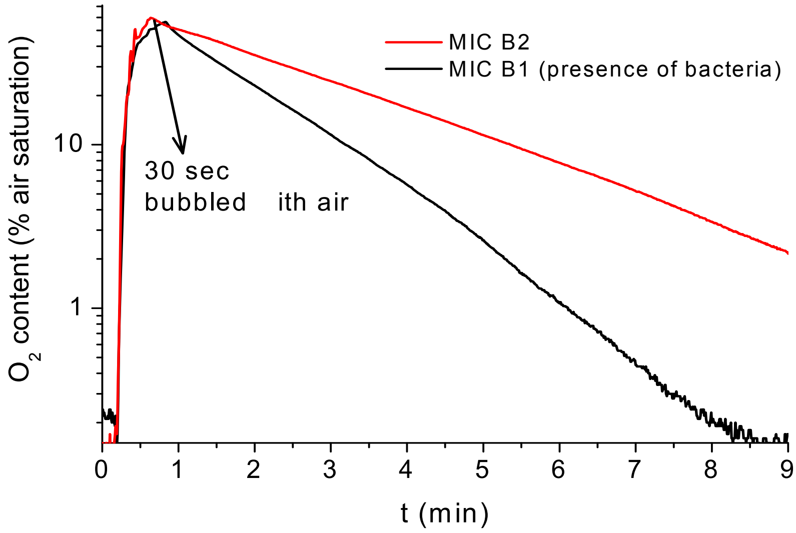
[1] upper limit

Table 1: Upper limits of oxygen concentrations determined with sensor type I.

Based on the experimental data recorded with sensor type 1, only upper limits for the oxygen concentration in the samples were calculated (see table 1).

From the time traces of the luminescence signal a quantification of the amount of O_2 carried over by the injection of the fiber tip into the sample can be estimated. Especially the MIC sample set showed a robust buffer capacity, valuable information on the carry over of oxygen (e.g., oxygen sorbed to the sensor surface or "in" polymer matrix) could be obtained from the time response function of the oxygen concentration after injection of the optode into the sample.

For the MIC samples their "intrinsic oxygen buffer capacity" was investigated as well. After stopping the oxygen bubbling, the oxygen concentration returned to its initial level. It is interesting to note that the kinetics of the "return" was dependent on the presence/absence of bacteria. The kinetics of the pure media were distinctly slower compared to the corresponding kinetics when bacteria were present in the sample.



ii) Oxygen measurements carried out using sensors of type II

The preliminary measurements using the prototype sensor (type II) were very intriguing and helpful to further optimizing the optical detection approach. During the ICE it turned out, that several technical parameters for oxygen measurements at the very low concentration range have to be adapted in the set up with sensor type II. Of the electronic components especially the modulation frequency generator needed to be adapted to modulation frequencies smaller than 1 kHz. In the set up used during the ICE a stable modulation at such low frequencies was not achievable, which limited the applicability with respect to the limit of detection (LOD) and the precision. In the current set up this has been optimized as a direct result of the ICE. The frequency range of the detection electronics has been adapted and with the current setup a precision in the oxygen determination better than 5 ppm can now be achieved.

The LOD determination with sensor type II was strongly influenced by the calibration procedure, which turned out to be a very crucial part since standard samples with well-defined oxygen concentrations smaller than 3 vol% were hardly available during the ICE (especially the "zero"-point turned out to be of utmost importance for calibration.) and the LOD was estimated to about 50 ppm. As a consequence a novel gas mixing station, which allows a precise gas mixing at concentrations << 3 vol/%.

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