

1 ACID SULFATE SOIL FIELD pH TESTS

KM Watling, CR Ahern and KM Hey

1.1 INTRODUCTION

The field pH (pH_F) and field pH peroxide (pH_{FOX}) tests have been developed for a rapid assessment in the field of the likelihood of acid sulfate soils. These tests are easy to conduct, quick, and have a minimum set-up cost. The field tests have been developed to give reasonable prediction for many soils (provided the tests are performed properly) whilst at the same time being relatively easy to perform with a minimal amount of equipment. Soil field pH tests provide a useful indication of the existing and potential acidity levels in the soil. Although these field tests may provide an indication of ASS presence, they are purely qualitative and do not give any quantitative measure of the amount of acid that has been or could be produced through the oxidation process.

Field pH tests should be part of any ASS investigation. The field pH tests (both pH_F and pH_{FOX}) should be conducted at 0.25 m intervals on the soil profile, ensuring at least one test per horizon. It is recommended that field tests be conducted on-site, in the field. If the tests can't be performed in the field on-site, tests should be conducted within 24 hours of soil sample collection, ensuring appropriate sample handling procedures (see Section B). Samples suspected of containing monosulfides should undergo field pH testing immediately in the field.

1.2 FIELD pH TEST (pH_F)

The procedure for the field pH test (pH_F) is outlined below:

1. **Calibrate battery powered field pH meter** according to manufacturer's instructions.
2. **Prepare the test tubes in the test tube rack.** Make sure the rack is marked with the depths so there is no confusion about the top and bottom of the profile. Use of separate racks for the pH_F and pH_{FOX} tests is recommended as contamination may occur when the pH_{FOX} reactions are violent. As the soil:water paste is inclined to stick to the walls of tubes, it is best to use shallow, broad test tubes as this makes cleaning easier.
3. **Conduct tests at intervals on the soil profile of 0.25 m or at least one test per horizon** whichever is lesser.
4. **Remove approximately 1 teaspoon of soil from the profile. Place approximately ½ teaspoon of that soil into the pH_F test tube and place ½ teaspoon of the soil into the pH_{FOX} test tube** for the corresponding depth test. It is important that these two sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take ½ teaspoon of soil from the 0–0.25m depth that is grey mud, while selecting ½ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
5. **Place enough deionised water** (or demineralised water if deionised water is not available; never use tap water) **in the pH_F test tube** to make a paste similar to 'grout mix' or 'white sauce', **stirring the soil:water paste** with a skewer, strong tooth pick or similar to ensure all soil 'lumps' are removed. Do not leave the soil samples in the test tubes without water for more than 10 minutes. This will reduce the risk of sulfide oxidation—the pH_F is designed to indicate the existing pH of a soil in the field; any oxidation subsequent to the soil's removal from the ground will not reflect the true field pH. In some instances, in less than 5 minutes, monosulfidic material may start to oxidise and substantially affect the pH_F results.

6. **Immediately place the spear point electrode (preferred method) into the test tube**, ensuring that the spear point is totally submerged in the soil:water paste. Never stir the paste with the electrode. This will damage the semi-permeable glass membrane.
7. **Measure the pH_F** using a pH meter with spear point electrode.
8. **Wait for the reading to stabilise and record the pH measurement.**
9. **All measurements should be recorded on a data sheet.**

1.3 FIELD pH PEROXIDE TEST (pH_{FOX})

It is recommended that 30% hydrogen peroxide (H_2O_2) be used in the pH_{FOX} test. 30% H_2O_2 is highly corrosive and care should be taken when handling and using the peroxide. Safety glasses and gloves should be worn when handling and using peroxide. All chemical bottles should be clearly labelled and Material Safety Data Sheets (MSDS) should be kept with the chemicals at all times. Appropriate health and safety precautions should be adhered to. Peroxide should be kept in the fridge when not in use.

The procedure for the field pH peroxide test (pH_{FOX}) is outlined below:

1. **Adjust the pH of the hydrogen peroxide to pH 4.5–5.5 before going into the field.** This can be done by adding a few drops of dilute NaOH stirring and checking the pH with the electrode regularly until the correct range is reached. NaOH is highly caustic so safety precautions must be exercised. NaOH can raise the pH quickly or slowly, so the pH needs to be monitored. Recheck the pH after allowing the peroxide to stand for 15 minutes. Do NOT buffer a large quantity of hydrogen peroxide at one time. Only buffer the amount to be used in the field for about a month. This must be kept in a fridge, well labelled with only small quantities to be taken into the field at one time. This will ensure the longevity of the peroxide. Further, over time, the pH of the peroxide that has already been buffered may change. It is important to check the pH of the peroxide in the morning before departing to the field. Having a small quantity of NaOH in the field kit is recommended so the peroxide can be buffered if required.
2. **Calibrate battery powered field pH meter** according to manufacturer's instructions.
3. **Prepare the test tubes in the test tube rack as for pH_F test.** Make sure the rack is marked with the depths so there is not confusion about the top and bottom of the profile. Use of separate racks for the pH_F and pH_{FOX} tests is recommended as contamination may occur when the pH_{FOX} reactions are violent. It is important to use **heat-resistant test tubes** for the pH_{FOX} test as the reaction can generate considerable heat (up to 90°C). It is recommended that a tall, wide tube be used for this test as considerable bubbling may occur, particularly on highly sulfidic or organic samples.
4. **Conduct pH_{FOX} tests at intervals on the soil profile of 0.25 m or at least one per horizon** whichever is lesser.
5. **From the teaspoon of soil previously collected for the pH_F test, place approximately $\frac{1}{2}$ teaspoon of the soil into the pH_{FOX} test tube** for the corresponding depth test. It is important that these two sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take $\frac{1}{2}$ teaspoon of soil from the 0–0.25m depth that is grey mud, while selecting $\frac{1}{2}$ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
6. **Add a few millilitres of 30% H_2O_2 (adjusted to pH 4.5–5.5) to the soil** (sufficient to cover the soil with peroxide) **and stir the mixture.** Do NOT add the peroxide to the test tube in which the pH_F test was conducted, that is, the pH_{FOX} test tube should not have any deionised water in it. Beakers can be used, however glass is usually easily broken when conducting field work, and when multiple tests are being conducted it is difficult to handle large beaker sizes efficiently. Do NOT add more than a few millilitres at a time. This will prevent overflow and wastage of

- peroxide. A day's supply of peroxide should be allowed to reach room temperature prior to use (cold peroxide from the fridge may be too slow to react).
7. **Rate the reaction of soil and peroxide using a XXXX scale** (see below and Table H1.1).
 8. **Ideally, allow approximately 15 minutes for any reactions to occur.** If substantial sulfides occur, the reaction will be vigorous and may occur almost instantly. In this case, it may not be necessary to stir the mixture. Careful watch will be needed in the early stages to ensure that there is no cross contamination of samples in the test tube rack. If the reaction is violent and the soil:peroxide mix is escaping from the test tube, a small amount of deionised water (or demineralised water; not tap water) can be added (using a wash bottle) to cool and calm the reaction. Usually this controls overflow. Do NOT add too much deionised water as this may dilute the mixture and affect the pH value. It is important to only use a small amount of soil otherwise violent reactions will overflow and the sample will be lost.
 9. **Steps 6 to 8 may be repeated** until the soil:peroxide mixture reaction has slowed. This will ensure that most of the sulfides have reacted. In the lab this procedure would be repeated until no further reaction occurs, however in the field, best judgement is recommended. Usually one or two extra additions of a few millilitres of peroxide are sufficient.
 10. If there is no initial reaction, individual test tubes containing the soil:peroxide mixture can be placed into a container of hot water (especially in cooler weather) or in direct sunlight. This will encourage the initial reaction to occur. When the sample starts to 'bubble', remove the test tube immediately from the hot water and replace into test tube rack.
 11. **Wait for the soil:peroxide mixture to cool** (may take up to 10 minutes). The reactions often exceed 90°C. Placing an electrode into these high temperature situations may result in physical damage and inaccurate readings. Check the temperature range of the pH meter and probe to see what temperature is suitable. Note that a more exact pH is achieved if a temperature probe is also used, however this may be impractical in some field situations.
 12. **Use an electronic pH meter (preferred method) to measure the pH_{FOX} .** Place a spear point electrode into the test tube, ensuring that the spear point is totally submerged in the soil:peroxide mixture. Never stir the mixture with the electrode. This will damage the semi-permeable glass membrane.
 13. **Wait for the reading to stabilise and record the pH_{FOX} measurement.**
 14. **All measurements should be recorded on a data sheet.**

a) Rating soil reactions of the pH_{FOX} test using the XXXX scale

The rate of the reaction generally indicates the level of sulfides present, but depends also on texture and other soil constituents. A soil containing very little sulfides may only rate an 'X' however a soil containing high levels of sulfides (remember the exact level of sulfides cannot be determined using the pH_{FOX} test) is more likely to rate a 'XXXX' although there are exceptions. This rating scale alone should not be used to identify ASS. It is not a very reliable feature in isolation as there are other factors including manganese and organic acids which may trigger reactions. Reactions with organic matter tend to be more 'frothing' and don't tend to generate as much heat as sulfidic reactions. Manganese reactions will be quite extreme, but don't tend to lower the pH_{FOX} . Table H1.1 indicates the reaction scale for pH_{FOX} tests.

Table H1.1 Soil reaction rating scale for the pH_{FOX} test.

Reaction scale	Rate of reaction
X	Slight reaction
XX	Moderate reaction
XXX	High reaction
XXXX	Very vigorous reaction, gas evolution and heat generation commonly $>80^{\circ}\text{C}$

1.4 INTERPRETATION OF FIELD pH TESTS

For details on how to interpret the field pH tests (pH_{F} and pH_{FOX}) please refer to the following references:

Ahern CR, Ahern MR and Powell B (1998). *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998*. Department of Natural Resources, Indooroopilly, Queensland, Australia. pp. 28–30.

Ahern CR, Stone Y and Blunden B (1998). *Acid Sulfate Soils Assessment Guidelines*. Acid Sulfate Soil Management Advisory Committee, Wollongbar, NSW, Australia. pp. 56–58.

Hey KM, Ahern CR and Watling KM (2000). Using Chemical Field Tests to Identify Acid Sulfate Soils Likelihood. In *Acid Sulfate Soils: Environmental Issues, Assessment and Management, Technical Papers*. Ahern CR, Hey KM, Watling KM and Eldershaw VJ (eds), Brisbane, 20–22 June, 2000. Department of Natural Resources, Indooroopilly, Queensland, Australia. pp. 16-9–16-12.

Hey KM (ed) (2002). *Field Testing, Sampling and Safety for Acid Sulfate Soils*. Department of Natural Resources and Mines, Indooroopilly, Queensland, Australia. pp. 12–16.

2 EFFERVESCENCE TEST ('FIZZ TEST') FOR CARBONATES

This test is used to determine the presence of carbonates in soil. It is a quick, easy, cheap test to conduct in the field. The test should be conducted on samples suspected of containing carbonates (eg. fine shell, crushed coral etc).

The procedure for the fizz test is outlined below:

1. **Place a small sample of soil (approximately one teaspoon) into a clear test tube.** Clear test tubes are preferred as this makes it easier to see any reactions. It is important that test tubes used in the fizz test are not used for the field pH tests as cross-contamination may occur, affecting pH readings.
2. **Place two or three drops of 1 M hydrochloric acid (HCl) onto the soil sample.** HCl is highly corrosive so safety precautions must be exercised.
3. **Rate the reaction** (see Table H2.1).
4. **All measurements should be recorded on a data sheet.**

Table H2.1 Soil reaction rating scale for the fizz test (as described in McDonald *et al.* 1990, pp. 147–148).

Reaction scale	Rate of reaction
N – non-calcareous	No audible or visible effervescence
S – slightly calcareous	Slightly audible but no visible effervescence
M – moderately calcareous	Audible and slightly visible effervescence
H – highly calcareous	Moderate visible effervescence
V – very highly calcareous	Strong visible effervescence

References

McDonald RC, Isbell RF, Speight JG, Walker J and Hopkins MS (1990) 'Australian Soil and Land Survey Field Handbook, 2nd Ed'. (CSIRO Publishing: Canberra)

