Rapid field test for carbonation of lime or cement treated materials

F Netterberg

Group: Soil Engineering (F Netterberg)
Branch: Roads Branch (R N Walker)

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Author

F Netterberg

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Soil Engineering Group
National Institute for Transport and Road Research
CSIR
P O Box 395
PRETORIA
0001
Republic of South Africa

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SYNOPSIS

A rapid field test for carbonation of lime, lime-slag, lime-PFA, cement, cement-PFA or cement-slag stabilized pavement material is described. The treated material is simply sprayed with phenolphthalein, phenol red and dilute hydrochloric acid solutions. If the untreated material does not contain carbonate (i.e. fails to effervesce with hydrochloric acid) and the treated material does not turn red with phenolphthalein, but turns red with phenol red and effervesces with hydrochloric acid, the material is carbonated. If the untreated material does contain carbonate (i.e. effervesces with hydrochloric acid and probably turns red with phenol red) and the treated material does not turn red with phenolphthalein, the material is probably carbonated. The phenolphthalein test can also be used to test for the presence or absence of lime or cement in a freshly treated material, but not for the amount present.

SINOPSIS

'n Snelveldtoets vir die karbonering van kalk, kalkslak, kalk-PFA, sement, sement-PFA of sementslak gestabiliseerde plaveiselmateriaal word beskryf. Die behandelde materiaal word eenvoudig met fenolftaleïen, fenolrooi en verdunde soutsuuroplossings gespuit. Indien die onbehandelde materiaal nie karbonaat bevat nie (dit is wanneer dit nie met soutsuur bruis nie) en die behandelde materiaal nie met fenolftaleïen rooi word nie, maar rooi word met fenolrooi en met soutsuur bruis, is die materiaal gekarboneer. As die onbehandelde materiaal karbonaat bevat (dit is wanneer dit met soutsuur bruis en waarskynlik met fenolrooi rooi word), en die behandelde materiaal word nie met fenolftaleïen rooi nie, is die materiaal waarskynlik gekarboneer. Die fenolftaleïentoets kan ook gebruik word om vir die teenwoordigheid of afwesigheid van kalk of sement in 'n pas behandelde materiaal te toets, maar nie vir die hoeveelheid wat teenwoordig mag wees nie.

This report supersedes the earlier report TS/16/82.

CONTENTS

1. INTRODUCTION

This is a rapid indicator test for carbonation of a layer which has been treated with lime, lime-PFA, lime-slag, cement, cement-PFA and cement-slag.

Phenolphthalein and phenol red change colour according to pH as follows (Notes 1 and 2):

Phenolphthalein:	pH	$\leqslant$ 8,3	9,0	$\geqslant$ 10
	colour	colourless	light red	red
Phenol red:	pH	$\leqslant$ 6,8	8,0	$\geqslant$ 8,4
	colour	yellow	orange-red	red

These colour changes are continuous, e.g. phenolphthalein starts to turn red above a pH of about 8,3, is a pale pink by 8,5, a dark pink or light red by pH 9 and has developed its deepest red colour by about pH 10,0.

Commercial hydrated lime is a mixture of calcium hydroxide($Ca(OH)_2$), magnesium hydroxide ($Mg(OH)_2$), and other substances. $Ca(OH)_2$ has a pH of about 12,4 and therefore turns red when sprayed with either of the above reagents. Unless partly or completely carbonated it does not effervesce with dilute hydrochloric acid. However, most commercial limes contain some carbonate (up to 9 % $CaCO_3$ equivalent is allowed in SABS 824) and do effervesce to some extent. $Mg(OH)_2$ only has a pH of about 10,4. Ordinary portland cement has a pH of 12,4 or more, and may also contain traces of carbonate (up to about 9 % $CaCO_3$ is effectively permitted by SABS 471, 626 and 831 and more may be allowed in the revised specifications). Cement releases lime on hydration. The active ingredient in unslaked lime (quicklime) is largely calcium oxide (CaO), which forms $Ca(OH)_2$ on slaking with water.

Calcium carbonate ($CaCO_3$) effervesces on addition of dilute hydrochloric acid. It has a pH of about 8,3 and therefore remains colourless with phenolphthalein, but turns red with phenol red. Calcium carbonate is present in many soils in arid, semi-arid and, to a much lesser extent, in dry subhumid climates. PFA and slag may also contain some lime and/or carbonate.

Sodium carbonate or bicarbonate occur in some arid zone soils. When present in amounts of about 0,1 % or more the former has a pH of more than 10,1 and therefore turns phenolphthalein red while the latter has a pH of 8,4 - 8,7 and therefore only turns phenol red red and phenolphthalein a barely noticeble pale pink. Both effervesce with acid when present in concentrations of more than about 0,5 %.

2. APPARATUS AND REAGENTS

Plastic wash bottles or other plastic dropper, squirt or spray bottles.

Phenolphthalein solution: prepare by dissolving 5 g of the reagent in 500 mℓ of ethanol (about 95 per cent pure), and add 500 mℓ of distilled water with constant stirring. Filter if a precipitate forms.

Phenol red solution: dissolve 0,1 g phenol red powder in 28,2 mℓ of a 0,01N NaOH solution (0,40 g NaOH/ℓ solution). Make up to 250 mℓ with distilled water.

Dilute hydrochloric acid (5N): dilute 430 mℓ of concentrated HCl to 1 ℓ with distilled water.

3. METHOD

Spray the full depth of the treated layer evenly with phenolphthalein until it is visibly wet, paying particular attention to interfaces and cracks. A red colour shows the pH to be > 8,3, suggesting that lime is present (Note 3). This lime may have been deliberately added or in the material itself (slag or PFA) or released by the hydration of cement. No colour change indicates the pH to be < 8,3, showing lime to be absent. This lime may have reacted with the material or have become carbonated. Excavate several more holes in the layer and repeat the test. Record the depths over which a red colour appears (Note 4).

Repeat with dilute HCl. Effervescence indicates the presence of a carbonate. Record the depths over which effervescence ceases or becomes markedly less.

Repeat with phenol red. A red colour indicates a pH of more than about 8,0, suggesting the presence of a carbonate, lime or cement. A yellow colour shows these substances to be absent.

If possible, test some of the original untreated material with the above reagents to confirm the absence of interfering compounds:

Phenolphthalein turns red: sodium carbonate, lime or cement. Possibly dolomite or sodium bicarbonate.

Phenol red turns red: calcium or sodium carbonate, sodium bicarbonate, dolomite or lime.

HCl effervesces: any carbonate (Note 5).

The layer can also be sampled in thin layers and analysed in a chemical laboratory for the percentage calcium carbonate. If carbonate was absent in the untreated material it will be found to be higher in the (carbonated) layers which did not turn red with phenolphthalein than those which did. The indicator colour changes can also be confirmed by means of laboratory pH measurements. Analysis for available lime by SABS 824 can also be carried out. These will show no available lime in the carbonated layers. For both tests the samples should be kept tightly sealed, dried preferably only in a vacuum desiccator, and resealed until tested. Conventional analyses for cement or lime content which measure the calcium and/or magnesium content are of no value except to show whether the stabilizer was ever added.

If the material turns red with phenolphthalein (it will also then turn red with phenol red), and also effervesces (usually only weakly) with acid, partial carbonation has taken place. Significant thicknesses of partially carbonated material appear to be rare, and the depths at which phenolphthalein turns red and effervescence with acid ceases are usually closely coincident.

Effervescence with acid is usually brisk in the carbonated part of a layer (i.e. more carbonate is present) and ceases or is greatly diminished when the part of the layer in which phenolphthalein turns red is tested. This has been confirmed by laboratory analyses for $CaCO_3$.

Carbonation from the bottom of a stabilized layer upwards, even after surfacing, has recently been recognised and can be similarly checked.

4. INTERPRETATION

If the untreated material did not contain lime, dolomite, sodium or calcium carbonate and the stabilizer also did not contain carbonates, but the treated material does not turn red with phenolphthalein, but turns red with phenol red and effervesces with HCl, the stabilizer and probably also any reaction products have become carbonated. If it turns yellow with phenol red and does not effervesce with HCl it is probably completely unstabilized (i.e. stabilizer destroyed e.g. by acid) or, more likely, the stabilizer was never added. If the treated material turns red with phenolphthalein and effervesces with HCl it is either partly carbonated and/or the untreated material contained carbonate.

If the treated material contained carbonate beforehand it is not possible to be certain by this method whether the stabilizer has become carbonated, only whether it has reacted in some way (either with the material or become carbonated). However, the current evidence is that if even a carbonate-containing stabilized material fails to turn red with phenolphthalein then the stabilizer is carbonated.

If it is not possible to check the untreated material for the presence of carbonate a reliable indication of whether or not the treated material is carbonated can still be obtained by spraying the acid over the area previously sprayed with phenolphthalein and noting the degree of effervescence. If the red coloured area shows significantly less (or none at all) effervescence than the apparently carbonated (i.e. uncoloured) area of the same layer, then the latter is carbonated, and the untreated material contained little or no carbonate.

Phenolphthalein is extremely sensitive and will turn bright red with as little as 0,2 per cent $Ca(OH)_2$ (Note 6). 5N Hydrochloric acid is also quite sensitive and will effervesce weakly in the presence of as little as 0,1 per cent $CaCO_3$, moderately strongly with 0,5 per cent and strongly with 1 per cent.

The general problem of carbonation has been discussed briefly by Netterberg and Paige-Green (1984).

5. NOTES

1. The above procedure uses easily available indicators which show good colour changes. They work well on calcretes and other light coloured materials. It is possible that other indicators may prove more useful with some coloured materials and may be more conclusive still. A fairly complete list of indicators is shown in Appendix A (Table A.1).

   Phenolphthalein is used in medicine as a purgative, usually in a dose of 50-300 mg (Todd, 1967). As the minimum dose of 50 mg would require ingestion of 10 ml of solution, the use of phenolphthalein as an indicator in the manner described is not likely to lead to any problems due to contamination of food, hands or mouth with a few drops of the solution. Phenol red is widely used in home swimming pool test kits and is presumably non-toxic. Dilute hydrochloric acid of 5N concentration should not be ingested and if spilt on the hands may lead to mild burns or irritation. If spilt on clothes, it may cause holes in the fabric. Possible toxic properties of the other indicators have not been investigated. As with all chemicals, they should be kept out of the reach of children, and the hands should preferably be washed after their use or before eating and certainly if any has been spilt on them.

   Some indicators are affected by some soils and yield false colours and more than one may be necessary. In choosing an indicator the colour of the soil relative to those of the indicator should be borne in mind. In general those changing from colourless to a bright colour or having two very different colours are better that those changing from say yellow to orange. In some cases it is necessary to also spray the material with water as a control. As shown in Table A.2, these are differences in opinion as to the exact pH indicated by a particular colour, and great accuracy should not be expected of this technique.

   Most of the indicators listed in Table A.1 have been evaluated by the author, and phenolphthalein is the only one of those tried which has so far been found to be apparently reliable in all the cases tried. In a few cases phenol red does not appear to have been satisfactory. However, in practice it is not always necessary and satisfactory results can usually be obtained using phenolphthalein and acid alone.

It should nevertheless be remembered that the reaction products in lime- and cement-soils mixes become unstable and liable to carbonate below a pH of 11-12 and not 10. The use of phenolphthalein alone is therefore not entirely safe, and acid should also always be used where practicable. For research purposes a higher indicator which will show whether the pH of the stabilized material is in excess of 11-12 is also desirable.

2. "Universal" indicator solutions (mixtures of several indicators) can be made up or purchased commercially which will change through a variety of colours at different pHs and can combine the value of e.g. phenolphthalein and phenol red.

Two suggested universal indicators which can be easily made up are as follows (Vogel, 1975):

1. 0,05 g methyl orange
   0,15 g methyl red
   0,3 g bromo thymol blue
   0,35 g phenolphthalein

   dissolve in 660 mℓ of 95 per cent ethanol and dilute to 1 ℓ with distilled water

pH	Colour
Up to 3	red
4	orange/red
5	orange
6	yellow
7	yellow/green
8	green/blue
9	blue
10	violet
11	red/violet

2. 0,1 g phenolphthalein
   0,2 g methyl red
   0,3 g methyl yellow
   0,4 g bromo thymol blue
   0,5 g thymol blue

   Dissolve in 500 mℓ ethanol (95 per cent) and add sufficient NaOH until the colour turns yellow.

pH	Colour
2	red
4	orange
6	yellow
8	green
10	blue

However, these indicators have not been found to be very satisfactory on soils and in practice only phenolphthalein, acid and phenol red are recommended at this stage.

3. The reaction is usually immediate although it may occasionally be necessary to wait for up to 30 seconds. Record whether immediate or not. Testing a soaked specimen, e.g. a UCS specimen, is not reliable as the lime migrates during soaking.

4. Before testing ensure that the material has not become contaminated with dust from digging. Brush or blow off if necessary.

5. Dolomite ($CaCO_3.MgCO_3$) effervesces more weakly than $CaCO_3$ with cold acid, but briskly with hot acid. It may have a pH of 8,6-10, i.e. more than $CaCO_3$, but has not so far been observed to turn phenolphthalein pink. It does, however, turn phenol red red. Magnesite ($MgCO_3$) is believed to behave similarly to dolomite, but this has still to be studied.

6. Phenolphthalein has also occasionally (since the 1960s in South Africa) been used to check for the presence or absence of lime in a lime stabilized soil and has more recently (Transportation Research Board, 1976; Nady and Handy, 1977) been suggested for checking the efficiency of mixing. A hole dug through freshly lime or cement

stabilized soil should turn red throughout, from top to bottom, when sprayed with phenolphthalein.

Note that this test only indicates the presence (more than about 0,2 per cent of lime) or absence of lime or cement, not the amount, and also that the hole must be freshly dug or cleaned back, since carbonation can proceed into the material at a rate of 1mm/day.

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APPENDIX A

INDICATOR SOLUTIONS

TABLE A.1: POSSIBLE INDICATORS FOR USE ON SOILS IN THE pH RANGE 5-13,6

Indicator	pH range	Critical pH[1]	Colour change	Reference
Acyl blue	12,0-13,6		Red-blue	Weast et al (1970)
Epsilon blue	11,6-13,0		Orange-violet	Merck Chemicals & Reagents (1974)
Malachite green[2]	1-11,5	1,0 & 11,5	Yellow-blue green-colourless	Weast et al (1970)
Tropaeolin O	11,1-12,7		Yellow-orange	Vogel (1975)
Parazo orange	11,0-12,6		Yellow-orange	Weast et al (1970)
Nitramine	10,8-13,0		Colourless-orange brown	Vogel (1975)
Brilliant cresyl blue (base)	10,8-12,0		Blue-yellow	Vogel (1975)
Alizarin yellow R	10,1-12,0	10,3	Yellow-orange red	Vogel (1975)
Tolyl red	10,0-11,6		Red-yellow	Weast et al (1970)
Phthalein red	8,6-10,2		Yellow-red	Weast et al (1970)
Thymolphthalein	8,3-10,5	9,4	Colourless-blue	Vogel (1975)
Phenolphthalein	8,3-10,0	8,3	Colourless-red	Vogel (1975)
Thymol blue[3]	2-8,0-9,6	1,9 & 8,9	Red-yellow-blue	Weast et al (1970)
Meta cresol purple	7,6-9,2	8,3	Yellow-purple red	Weast at al (1970)
Cresol red	7,2-8,8		Yellow-red	Weast et al (1970)
Phenol red	6,8-8,4	7,3	Yellow-violet red	Vogel (1975)
Neutral red	6,8-8,0		Red-orange	Vogel (1975)
Bromothymol blue	6,0-7,6	6,9	Yellow-blue	Vogel (1975)
Azolitmin (litmus)	5,0-8,0		Red-blue	Vogel (1975)

Notes: (1) The pH of most pronounced colour change (Jackson, 1958; p. 52).

(2) Decolourizes irreversibly above pH 11,5 (Jackson, 1958), is a blue green colour between about 1-11,5, and yellow below about 1.

(3) Red below about pH 2, yellow between about pH 2-8 and blue above about 9,6.

TABLE A.2: PH OF MAXIMUM COLOUR OF SOME INDICATORS ACCORDING TO DIFFERENT SOURCES

Indicator	Vogel (1975)	Weast (1970)	Medicines Commission (1980)	Label bottle
	Maximum colour at pH of:			
Phenol red	6,8- 8,4	6,6- 8,0	6- 9	6,4- 8,2
Brilliant cresyl blue (base)	10,8-12,0	-	-	10,8-12,0
Thymolphthalein	8,3-10,5	9,4-10,6	8-12	9,3-10,5
Bromo thymol·blue	6,0- 7,6	6,0- 7,6	5- 8	6,0- 7,6
Azolitmin (litmus)	5,0- 8,0	-	4- 9	-
Neutral red	6,8- 8,0	6,8- 8,0	6- 9	-
Phenolphthalein	8,3-10-0	8,2-10,0	7-11	8,2- 9,8
Universal (1)	3 -11	-	-	-
Universal (2)	2 -10	-	-	-

Compiled by C V Mason-Jones and F Netterberg

APPENDIX B

CONDENSED INSTRUCTIONS FOR CARBONATION FIELD TEST KIT

NATIONAL INSTITUTE FOR TRANSPORT AND ROAD RESEARCH
CARBONATION TEST KIT

1. REAGENTS

0,4 % Phenol Red : yellow at pH < 6,8 deepest red at pH ⩾ 8,4
0,5 % Phenolphthalein: colourless at pH ⩽ 8,3 deepest red at pH ⩾ 10
Dilute HCℓ (5N) : effervesces in presence of $CaCO_3$

2. METHOD

Excavate hole in layer to the full depth to be tested. Clean sides of hole by brushing or blowing. Spray side of hole to full depth with reagents in turn(1). The acid may be sprayed over one of the other reagents, usually the phenolphthalein, if desired. Repeat the test on the unstabilized material and the stabilizer if available(2).

3. PRINCIPLE OF METHOD

Lime or cement present: both phenol red(3) and phenolphthalein turn red.
$CaCO_3$ present : phenol red(3) turns red and HCℓ effervesces.

4. INTERPRETATION

Carbonation absent(4) (red colour with phenolphthalein)

(a) $CaCO_3$ absent from original materials: red colour with phenolphthalein (phenol red should also turn red) and no effervescence with acid.

(b) $CaCO_3$ present in original material(s): red colour with phenolphthalein (phenol red should also turn red) and effervescence with acid. In this case partial carbonation(4) cannot be ruled out.

Complete carbonation(4) (no colour change with phenolphthalein)

(a) $CaCO_3$ absent from original materials: no colour change with phenolphthalein, but red with phenol red, and effervescence with acid.

(b) $CaCO_3$ present in original material(s): as for (a). However, cannot be certain whether carbonated or stabilizer never added.

Stabilizer never added (no colour change with phenolphthalein)

(a) $CaCO_3$ absent from original materials: no colour change with phenolphthalein, and absence of effervescence with acid.

(b) $CaCO_3$ present in original material(s): no colour change with phenolphthalein, but red with phenol red, and effervescence with acid. However, cannot distinguish whether carbonated or stabilizer never added.

In both cases a yellow colour with phenol red is strong additional evidence that the stabilizer was never present.

5. WARNING

Phenolphthalein is a powerful laxative - wash hands after use or before eating. HCℓ will eat holes in clothing.

6. REFERENCES

NITRR Reports RS/2/84 and RS/3/84.

NOTES

1. Carbonation attacks the stabilized material as a "front" at all interfaces with atmospheric or soil CO_2, e.g. an exposed layer, contacts with permeable unstabilized layers, and crack faces. All such surfaces should therefore be checked.

2. This is often not possible, However, if the stabilized material which now turns red with phenolphthalein does not effervesce with acid (i.e. $CaCO_3$ absent), then $CaCO_3$ was absent in the original materials. If it effervesces, the $CaCO_3$ may be due to carbonation and/or have been in one or both of the original materials (soil and/or stabilizer). If the effervescence is weaker in the red material than in the uncoloured material, the uncoloured material has probably been carbonated. In many cases a reasonable guess can be taken as to whether the untreated soil contained carbonate, while it should be remembered that limes and cements are not always carbonate-free and <u>may</u> contain up to about 10 % $CaCO_3$.

3. Phenol red cannot always be relied upon to give clearly discernible colour changes. However, in practice phenolphthalein and acid are usually sufficient.

4. Provided that $CaCO_3$ was absent from the original materials <u>partial carbonation</u> is indicated by a red colour with phenolphthalein and effervescence with acid. Significant amounts or thicknesses of partially carbonated material seem to be rare.

OTHER POSSIBLE USES FOR TEST KIT

1. <u>Mine rock crushed stone base material</u> (see RR 260)

   (a) Yellow with phenol red: danger of salt damage - check conductivity and pH.

   (b) Red with phenolphthalein: lime or cement was added - no danger of salt damage.

   (c) No colour change with phenolphthalein, but red with phenol red and effervesces with acid: lime added, but it carbonated - check conductivity.

2. <u>Dispersive soils</u> (see Ground Profile, Jan. 1980. p. 16 and USDA Handbook 60, p. 18)

   (a) Red with phenolphthalein: ESP probably > 15, therefore probably a dispersive soil. (This does not apply to stabilized materials.) Failure to turn red does not mean that the soil is non-dispersive.

3. <u>Deteriorated cement or lime</u>

   Fails to turn red with phenolphthalein, and effervesces strongly with acid: completely deteriorated - do not use.

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