

# THE REAL CAUSE OF DETRIMENTAL CARBONATION IN CHEMICALLY STABILIZED LAYERS AND POSSIBLE SOLUTIONS

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## ABSTRACT

Up till very recently detrimental “carbonation” of cement and lime stabilized layers in Southern Africa, which normally manifests itself in the form of a thin loose powdery layer on the stabilized layer surface, was perceived to be caused by poor and/or insufficient curing. It was perceived that “carbonation” could be controlled through continuous water curing for 7 days and by working the stabilized layer over optimum moisture content during construction. If not kept wet the theory would have it that the layer “carbonated” in the presence of CO<sub>2</sub> from the air causing the powdery layer to form. It was also assumed that if the layer is tested for pH and the pH was found to be low that the un-stabilised layer of material was brought in from the windrows. These causes were all seen by earlier researchers as construction related problems for which contractors were held responsible to make good. This has recently lead to catastrophic failures on a number of large projects in the Southern African region, leading to tremendous costs for all parties involved. However, in depth research on the chemically stabilized materials from a number of problem projects by the authors, simulating site construction constraints and ambient conditions in the presence of water and absence of CO<sub>2</sub>, have lead them to believe that the real cause of the problem is a water driven reaction with the material, which is beyond the control of the Contractor, as he neither selected the material or proposed the design. The dormant reaction was never described correctly, because presently used stabilisation design testing techniques do not simulate conditions on the construction sites. The only way in which these detrimental reactions will be identified correctly prior to the construction phase, is by simulating the site construction constraints and ambient conditions. This paper deals with the basic fundamentals of carbonation and how to determine the other reaction that may take place in the material.

## KEYWORDS

CARBONATION/ CHEMICAL REACTIONS/ WATER CURING/ NEW TESTING PROTOCOL

## 1 INTRODUCTION

This paper deals with the problems related to the “curing” of the stabilized layers, after the initial construction phase to prevent “carbonation”. The curing techniques that were followed in the presence of water but absence of CO<sub>2</sub> very clearly pointed to the fact that the “detrimental carbonation “ reaction is water driven rather than CO<sub>2</sub> driven. In actually fact the so-called “detrimental carbonation” chemical reaction cannot even take place without free water being available. The water is normally supplied by the specified curing

technique to keep the layer moist for at least 7 days. Furthermore, this water driven reaction may in some cases continue long past the original construction period (up 60 days), showing that the Initial Consumption of Lime (ICL) as measured in the laboratory, is often not enough to satisfy the Extended Consumption of Lime (ECL). Where this loose layer was swept off after initial construction on site, it was found that a new loose layer often formed below the prime and surfacing. This was normally blamed on over-rolling the surfacing layer during construction (so-called material breakdown, or not sweeping properly before priming, for which the Contractor was once again held responsible).

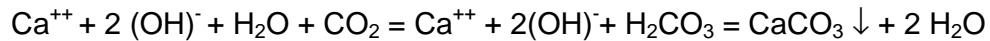
With this new understanding of “carbonation” that has become available the time has come where the civil engineering industry should realize that if the specified construction technique is not working, that the problem might be material related and not construction related. While the Authors agree that Contractors are not always blameless, it would be in the interest of the industry in general to tackle undefined problems together as Client, Engineer and Contractor together in order to solve the problem swiftly and as costs effectively as possible.

## 2. CHEMICAL REACTIONS DURING CARBONATION

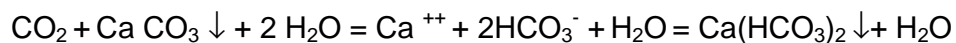
The carbonation reaction requires the presence of water to participate in the reactions. The water acts as a carrier medium to convey the carbon dioxide to the slightly soluble calcium hydroxide. Two parallel reactions are taking place at the same time, namely water-driven and carbonation reactions (CO<sub>2</sub>) (Paige-Green et al, 1990):

### 2.1 Carbonation reaction

The carbon dioxide is dissolved in the water forming a weak acid that can dissolve the available calcium hydroxides (Paige-Green et al, 1990).



If more CO<sub>2</sub> is available then



If the pH drops below 10 to approximately 8,5 the destruction of the Calcium Silicate Hydrate (CSH) and Calcium Silica Aluminates (CSA) will follow. The situation ends up with a pH below 8,5 (Paige-Green et al, 1990).

### 2.2 Water-driven reactions

$\text{Ca}^{++} + 2 (\text{OH})^{-} + \text{H}_2\text{O} + 2\text{Na}^{+}$  (iron exchange if all the clay present in the material has not reacted) forming  $2\text{Na}^{+} + 2 (\text{OH})^{-}$  (Foster, 1953)(from Eggimann et al, 1980) which aggressively attacks the alumino silicates, and fine-grained quartz, destroying the cementitious bonds. This reaction can take place without the presence of CO<sub>2</sub>. If more  $\text{Ca}^{++} + 2 (\text{OH})^{-}$  is available new Calcium Silicate Hydrate (CSH) and Calcium Silicate Aluminates (CSA) can form that can destroy the existing cement matrix by expansion. The pH could also drop due to depletion of the  $\text{Ca}^{++} + 2 (\text{OH})^{-}$ .

Both Paige-Green et al (1990) and Clauss (1988) described these reactions. Unfortunately the water driven reaction was not considered as part of the existing carbonation theory. It must however be pointed out that the carbonation reactions require water to be freely available to complete the reactions (CO<sub>2</sub> + H<sub>2</sub>O).

The lime demands shown in Table 1 (from site where failures occurred) were determined for Hopetown and Heidelberg (Semmelink, 2001). In all three cases these samples came from a road that had previously been stabilised, indicating that the full lime demand had not been met originally, or that with time the lime demand had increased / returned.

Table 1 - Laboratory determined lime demands on previously stabilized samples from Hopetown (Semmelink et al 2001)

Sample Number	Starting pH	Lime demand [percentage]	Lime demand for total sample [percentage]	Ordinary Portland Cement (OPC) demand for total sample [percentage]
JR3938/1	12,5	1,5	0,97	1,19
JR3938/2	13,25	1,5	0,90	1,11
JR3945	11,2	1,5	0,76	0,93

### 2.3 Water driven reactions in the absence of CO<sub>2</sub>

During ion exchange  $\text{Ca}^{++} + 2 (\text{OH})^- + \text{H}_2\text{O} + 2 \text{Na}^+ = 2 \text{Na}^+ + 2 (\text{OH})^-$  is formed in the reaction of  $\text{Ca}(\text{OH})_2$  with the clay minerals. The NaOH is relatively soluble and can be transported to just under the surface of a sealed road due to hydro-genesis. Furthermore, the NaOH is also relatively hygroscopic and thus it will attract water once formed, which will increase the ability to migrate. The solubility of the different compounds formed by the reactions is provided in Table 2.

Table 2 - Solubility of the selected compounds in gram per 100ml of cold water (Weast, 1975).

Compounds	Solubility [g/100ml]
$\text{CaCO}_3$	0,0014
$\text{Ca}(\text{HCO}_3)_2$	0.1
$\text{Ca}(\text{OH})_2$	0,185(at 0 °C)*
NaOH	42,0

\* Solubility increase due to the presence of CO<sub>2</sub>. Lime water becomes clear when carbon dioxide is bubbled through the milky water, the  $\text{Ca}(\text{OH})_2$  in the water is dissolved.

The ion exchange reaction if all the clay has not reacted is indicated by  $\text{Ca}^{++} + 2 (\text{OH})^- + \text{H}_2\text{O} + 2 \text{Na}^+$  and forms  $2 \text{Na}^+ + 2 (\text{OH})^-$  (Foster, 1953). The NaOH then aggressively attacks the aluminosilicates and fine-grained quartz, destroying the cementitious bonds. This reaction can take place in the absence of CO<sub>2</sub>. If more  $\text{Ca}^{++} + 2 (\text{OH})^-$  is available, new Calcium Silica Hydrates (CSH) and Calcium Silica Aluminates (CSA) can form that can destroy the existing cement matrix by expansion. The pH could also drop due to depletion of the  $\text{Ca}^{++} + 2 (\text{OH})^-$  and H<sub>2</sub>O. Due to the high solubility of NaOH and its ability to migrate to the interlayer between the base and the surfacing, the surfacing layer may still maintain a relatively high pH. This relatively high pH and relatively dry layer underneath the surfacing layer was observed on four problem sites where carbonation was indicated to have occurred (see Figures 1 to 4 from the Hopetown site, Northern Cape Province, South Africa). This surface developed after water curing and brooming (Figure 1) of the loose material. Figures 2 and 3 show the same surface a few months later after sealing. On a site under similar conditions where the water curing was left out leaving the top surface remained intact.

#### 2.4 Water driven reactions in the presence of CO<sub>2</sub>

However, when CO<sub>2</sub> is present, the CO<sub>2</sub> acts as an accelerator, dissolving Ca<sup>++</sup> + 2 (OH)<sup>-</sup> in the presence of water would continue and react with the available clays not treated yet, as the Ca(OH)<sub>2</sub> is crowding the clay particles. Ion exchange Na<sup>+</sup> for Ca<sup>++</sup> and the 2 Na<sup>+</sup> + 2 (OH)<sup>-</sup> can then take place to react as described by Foster (1953). In this soluble state the new CSH and CSA can form. Both these reactions are relatively rapid. The compound that is formed is also relatively sensitive to pH level and may be transient at a pH below approximately 10,5. It appears to be permanent as long as the pH is maintained above 10,5 (Lea, 1970). If the pH dropped from 12,5 to 9,0, which would indicate that too little lime was available, this could lead to the decomposition of the semi-stable CSH phases I and II (Lea, 1970).

The reactions associated with this dry layer can be described as follows (Scholtz, 1987) using the Blaschke Model, during phase the pH was above 12,5 the following can occur: "The alkaline solution secreted from the hardening (shrinking) cement erodes the aluminosilicate-glass. The solvated material is settled out on the phase border consisting if Ca-rich OPC glue generating a hydrogel of A1-silicates. Because of the Na/K contents of the smectite glass, it can be classified as a Na/K A1-Si-Hydrogel. These hydrogels are well known for their extremely high absorptive powers. Its specific surface is in the range of a few hundred square meters per gram".

This reaction is an internal chemical reaction between alkalis generally derived (and can thus also be generated from the material that is stabilised) from the cement or cement reactions with the surrounding material, and amorphous/ micro-crystalline/ altered forms of silica in the aggregate. A hygroscopic, expansive gel is produced which swells when exposed to excess water (Alexander, 1987).



Figure 1 - View of the broomed surface of stabilised base showing coarse finish after removal of fines which did not stabilise and compact just before priming and sealing, shortly after stabilisation before priming and surfacing (taken at the time of construction)(Simmelink et al, 2001)



Figure 2 - The dry layer under the Bitumen-Rubber seal is shown in the photograph, limited CO<sub>2</sub> exposure and a built up of moisture under the seal has created this condition. The carbonation tests show that no carbonation took place, the dry condition shows the destructed top portion of the layer (Semmelink et al, 2002)



Figure 3 - The stabilised layer shows no signs of the carbonation reaction, note how dry the surfacing is (Semmelink et al, 2002)

The failure shown in Figure 1 occurred at Heidelberg, Mpumalanga Province, South Africa where the dolerite was stabilised with foam bitumen and cement (Semmelink et al, 2001). The recycled base course was accepted after initial construction for placing the medium continuous asphalt. 14 days later the base showed signs of deterioration as seen in Figure 5.

This drop in pH can be demonstrated by the extended ICL/ ICC and water driven process where the CO<sub>2</sub> is excluded and only water is provided (Figure 5) produced a failed surface similar to that found in the field after 7 days ambient curing.

At Soutpan near Bloemfontein, Free State Province, South Africa, the water reactive phase of the reaction was controlled by using anionic emulsion stabilisation in combination with cement (Botha, 2003). The reactive clay minerals in the material were coated by the added 2,5 percent anionic emulsion and stabilised by the 1,5 per cent cement. No traditional detrimental carbonation problems were seen on site although the reactive clay mineral counts were higher than at sites in Heidelberg and Hopetown (Semmelink et al, 2001).



Figure 4 - Close-up view of surface of recycled weathered dolerite surface where the surfacing broke loose showing the loose material

A so-called carbonation failure of calcrete in the Caprivi Strip, Namibia (Botha, 1999) was repaired by a further dilution of 4.5 per cent anionic emulsion SS20 that was added to the calcrete together with 3,0 per cent cement. The initial failure that occurred on the half width of the road over a length of 25 km was due to the emulsion that had not been diluted enough and stable enough to coat all the reactive minerals.

From these two cases (Soutpan and Caprivi) enough evidence is available to prove that the detrimental water driven reactions can generally be controlled. From carbonation investigations done on site it can be further concluded that if the water reaction are controlled by emulsion coating that the carbonation is no longer detrimental but follows the normal pattern of strength gain as seen in the test results (see Table 3).

On another site at Bochum, Limpopo Province South Africa with similar clay composition the dry-hydro-gel formation was controlled by changing from a CEM I 42,5 (OPC) to CEM II B-S 32,5 so that the alkaline reaction as postulated by Scholtz and Alexander was seemingly controlled by the addition of granulated blast furnace slag obtained from the steel manufacturing process (blast furnace as well as the corex process) (Botha, 2005). From this it is concluded that the detrimental chemically reaction has been identified correctly.

Naturally it would be in the interest of all parties if these detrimental reactions were identified prior to the construction of a road so that they can be addressed properly in the design phase of the project. In order to do this a design procedure has been developed by the authors in order to investigate the material's reaction to the specified design procedure or preferably to select a stabilization procedure which will avoid failures on site if possible.

These cases all confirm the earlier finding of Paige-Green et al (1990): "Carbonation has been confirmed or is strongly indicated to have been a factor in about half of the cases. In the remainder of cases the available information does not permit an assessment of whether or not carbonation was involved." It seems from the results in Table 3 that carbonation is more strength gaining rather than strength reducing. This more in line with Ludloff (1979) about the role of water in concrete.

Table 3 - Example of results of Caprivi calcrete after stabilization and testing in CO<sub>2</sub> bomb (Small, 1999)(page 3)

General Information							Mod.AASTHO Data		Specimen Data								Strength Relationship		
Date	Position (km)	Lab.No.	G.M.	Cement Content (%)	Emulsion		MDD (kg/m <sup>3</sup> )	OMC (%)	Moulding MC (%)	UCS (kPa)						Mass Change after Carb (%)	7 Day % 24h	Carb % 24 h	Carb % 7 Days
					Type	(%)				Cured 24h @70 °C		Cured 7 Days		Cured 24h @ 70 °C Carb					
				Actual	@100%	Actual	@100%	Actual	@100%										
17/07/99	3+340-3R	993	1.96	3.0	SS20	5.4	1734	12.2	11.8	3048	3045	2313	2305	3137	2971	1.2	75.7	97.6	128.9
Proctor Effort										1835		1375		1554		1.1			
17/07/99	3+470-5R	998	1.41	3.0	SS20	5.4	1756	11.9	12.9	1985	1960	1454	1411	1786	1760	0.2	72	89.8	124.7
Proctor Effort										1494		665		1532		0.3			
19/07/99	3+570-5R	1004	1.47	3.0	SS20	5.4	1726	12.7	12.8	2259	2467	1758	1712	2454	2495	1.2	69.4	101.1	145.7
Proctor Effort										823		929		965		1.3			
19/07/99	3+680-5R	1007	1.27	3.0	SS20	5.4	1726	13.2	11.9	1442	1426	1220	1189	2195	2029	0.5	83.3	142.1	170.6
Proctor Effort										1050		756		728		0.6			
20/07/99	3+800-5R	1011	1.36	3.0	SS20	5.4	1731	13.4	13.7	2409	2168	1615	1432	2535	2239	0.5	66.1	103.3	156.4
Proctor Effort										1262		981		1446		0.5			
20/07/99	3+940-4R	1015	1.64	3.0	SS20	5.4	1750	12.6	12.5	2734	2727	2138	2116	2477	2473	0.2	77.6	90.7	116.9
Proctor Effort										1767		1164		1589		0.5			
21/07/99	4+060-4R	1030	1.97	3.0	SS20	5.4	1781	11.8	14	3192	3616	2807	2914	3088	3275	1.3	80.6	90.6	112.4
Proctor Effort										1389		1339		1468		1.1			
21/07/99	4+180-4R	1033	1.78	3.0	SS20	5.4	1640	14.9	14	2347	2133	1980	1782	2401	2180	0.2	83.5	102.2	122.3
Proctor Effort										1448		1137		1408		0.3			
21/07/99	4+240-3R	1036	1.98	3.0	SS20	5.4	1618	16.4	18.1	1318	1345	1174	1155	1564	1636	0.2	59.9	121.6	141.6
Proctor Effort										958		774		913		0.3			

### 3. SIMULATING SITE CONDITIONS

During the technical audit field investigation of the Hopetown site, the lowest densities found for the 0 – 50 mm and the 50 –200 mm layers were 90% and 98% modified AASHTO respectively. Erosion beams were manufactured using these densities. The two beams cured under simulated site conditions by placing the beams in sealed stainless steel chambers with sufficient curing water and placing them in the direct sunlight during the day for 6 days, were compacted to 90% and 98% of Mod AASHTO respectively. Both other beams compacted to 98% of Mod AASHTO. One was cured as per standard test method using rapid oven-curing in a sealed chamber with free moisture at 72 °C for 6 days, and the other sealed beam with free moisture was placed in a constant humidity room at 25 °C for 6 days (Semmelink et al, 2002).



Figure 5: A similar loose layer formed in the top layer of the two samples. This is the water simulated process without the presence of CO<sub>2</sub> done in the laboratory (Semmelink et al, 2002)



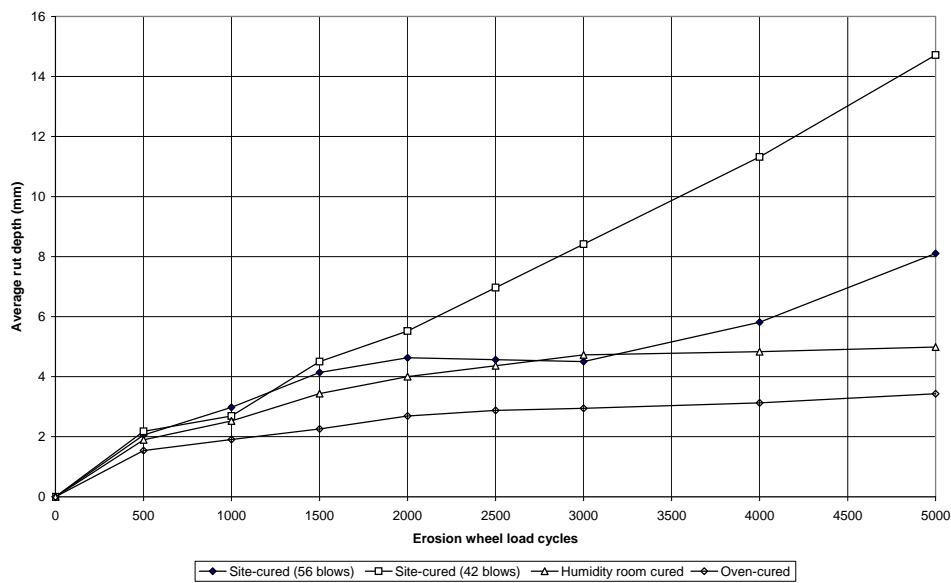
Photograph 6: Site cured beam (56 compaction hammer blows), site cured beam (42 compaction hammer blows) and humidity room cured beam prior to erosion beam test showing the dark pink colour stain of the phenolphthalein solution (Semmelink et al, 2002)



**Table 4: UCS estimates of the stabilized strength of each of the four beams**

	Site curing	Site curing	Oven curing	Humidity room curing
Compaction energy	(56 blows)	(42 blows)	(56 blows)	(56 blows)
	98%mod	90%mod	98%mod	98%mod
	Load (kN)	Load (kN)	Load (kN)	Load (kN)
Cube 1	2	3.9	28.5	7.5
Cube 2	2	1	24.5	9.5
Average load	2	2.45	26.5	8.5
Average UCS (kPa)	356	436	4711	1511

Figure 7 shows the erosion results of the four beams in graphical format.



**Figure 63: Erosion rut depth against number wheel load cycles for the four beams**

The four beams were tested and the outcome of the test results is graphically displayed in Figure 63. The erosion loss measurements of all the samples were already beyond the proposed maximum specification loss of 0.5 mm after the first 250 cycles. From this it can be deduced that the prescribed stabilizing agent produced a sub-standard stabilized layer with a long-term durability problem built into it by the design.

The simulated site surface samples gave UCS values very similar to the results found with the DCP in the 0 to 50mm portion of the constructed layer. However, the humidity-room-cured sample gave an acceptable USC value with predicted 28-day strength of 2.115 MPa (i.e. 1.4 times the 7 day strength of 1.511 MPa). In the case of the oven-cured sample the available pozzolanic material reacted with the cement to produce high strengths of 4.711 MPa, which is 3 times as high as the 7-day results normally used in stabilization. The tremendous variation in strength and erosion levels (see Table 4 and Figure 7), show that curing conditions (i.e. temperature and moisture content) and dry density levels of the material have a tremendous influence on the performance of the material.

## 4 CONCLUSIONS

The following can be concluded:

- That an alternative destructive water driven reaction was identified that is taking place parallel to carbonation. The carbonation reactions were found to enhance strength development, which brings it into line with normal carbonation reaction that is found in concrete (slow long term reactions).
- This destructive reaction does not require CO<sub>2</sub> but water; the CO<sub>2</sub> acts as an accelerator dissolving Ca(OH)<sub>2</sub> more readily. The reaction with Ca(OH)<sub>2</sub> is a very fast reaction.
- That the loss of stabilizer can be monitored by the extended ICL/ICC test, which is done in the absence of CO<sub>2</sub> but in the presence of water.
- That the failure can be simulated in the laboratory by simulating site temperatures in the absence of CO<sub>2</sub>, using newly developed testing protocol.
- Because the reaction is water driven, that water curing cannot control this reaction.
- This reaction thus cannot be stopped by mechanical means as it is not construction related but material related. Currently it is wrongly suggested that destructive carbonation can be controlled by means of water curing and working the material over optimum moisture content (Paige-Green et al, 1990).

## 5 RECOMMENDATION

The stabilization technology must be updated to make provision for this new approach to determine possible destructive reactions that occur in the field. The problem must be solved using the appropriate stabilizer design testing techniques that can control the problematic clay minerals. The current design techniques must be upgraded to identify the site problem in the laboratory by using site curing temperatures and curing techniques and newly developed testing protocol.

## REFERENCES

Addis, BJ. 1987. Portland Cement, Milled Granulated Blastfurnace Slag, Fly Ash, and Silica Fume: Development and Properties. Johannesburg, Practical guidelines on the selection and use of Portland cement, mgbs, fly ash and silica fume in concrete. xxx

Addis, B. 1997. Cement Concrete & Mortar, ISBN 0 9584085 2-1, Cement and Concrete Institute Midrand.

Amtsbuchler, R. 1987. Effect of Different curing regimes on fly ash concrete. Pretoria, Ash a valuable resource, Volume 2 concrete, February 1987.

Alexander, MG. 1987. Properties of Concrete and the constituent materials which necessitate the provision of joints in structures. Johannesburg, Joint in concrete structures, Mach 1987.

Botha, PB. 1999. The revised stabilisation design for the calcrete gravel base layer on Trunk Road 8, phase II extension. Pretoria, CSIR Transportek (Contract Report CR-99/037).

Botha, PB. 2005. Stabilisation investigation of borrow pit B between Bochum and Steilloop. Test Report

Clauss, KA. 1988. Natural, Low Cost Road construction Materials: Their Occurrence and Stabilisation. ISBN:0 620 1181 4 8 Pretoria 1988.

Eggimann, DW., Manheim, FT. and Betzer, PR. 1980. Dissolution and analyses of Amorphous Silica in Marine Sediments. Journal of Sedimentary Petrology. Volume 50. No.1 March, 1980.

Paige-Green, P., Netterberg, F. and Sampson LR. 1990. The carbonation of chemically stabilised road construction materials: guide to its avoidance. Pretoria, CSIR Transportek (Project Report 89/146/1)

Scholz, H. 1987. Fly Ash in Concrete Technology. Pretoria, Ash a valuable resource, February 1987.

Semmelink, CJ. and Botha, PB. 2001. Investigation into the causes of failure of a portion of the road R29 (Hopetown –Strydenburg). Pretoria, CSIR Transportek (Laboratory Report LR-2001/1/3938)

Semmelink, CJ. and Botha, PB. 2002. Evaluation of data and material from Trunk Road TR13 between Hopetown and Brak River that was made available to Raubex Construction (Pty) Ltd by the Northern Cape Province. Pretoria, CSIR, Transportek (Contract Report CR-2002/56)

Weast (see Clauss K A)

Loedolff G F 1977. Die rol van water in beton. Nasou Kaapstad, Nasou, (ISBN 0625014456)