#### CHAPTER 4

# Mixing Water

#### EFFECTS OF IMPURITIES

This Chapter deals with the effects on concrete of substances in the mixing water. The question of deleterious substances in aggregates has been considered in a previous section, but the two sections should be considered together, because the effects on the final concrete of impurities in the water and in the aggregates are cumulative. An aggregate which might safely be used with a pure water may be undesirable when used with a mixing water containing deleterious matter, especially if it is of the same type as that in the aggregate: for example, aggregates containing pyrites may become dangerous when used with a sulphate-bearing mixing water. This section does not deal with effects of different agents on hardened concrete.

The effect of impure waters on the concretes made with them varies markedly with the type of cement used for concrete-making. The effect of an aggressive agent on high alumina cement, or on pozzolanic cement will obviously be very different from that of the same agent on portland cement.<sup>1</sup>

In this note, only portland cement concretes will be dealt with, but it must be stressed that even within this range the effect of an aggressive water will depend on the cement used, and on the richness of the mix.

It might be well to sound, at the outset, a note of reassurance. In 1924 Professor Duff Abrams undertook exhaustive tests of some 68 waters including sea, alkali, mine, mineral and bog waters, and highly polluted sewage and industrial wastes.<sup>2</sup> He came to the conclusion that in spite of the origin and type of water used, and contrary to accepted opinion, most of the samples gave good results in concrete.

None of the waters tested caused unsoundness, and, with a few notable exceptions, the time of setting of the concrete was unaffected, although the latter must be regarded as an unsafe guide to the suitability of the water for concrete making.

Professor Abrams concluded that "neither colour nor odour is any indication of the quality of water for mixing with concrete. Waters which were most unpromising in appearance gave good results".

Dr. G. W. Bond, whose survey of the Republic's water supplies is a standard text,<sup>3</sup> stated "it is clear that, with the possible exception of some of the highly mineralized waters of the North West Cape Province and South West Africa . . . the majority of the Union's brackish waters could be used with impunity for concrete-making".<sup>4</sup>

It has also been established that some waters which over a period would be destructive to hardened concrete can be used without harmful effect for mixing purposes. This can be appreciated when it is realized that even with a water considered as highly polluted the total amount of deleterious matter in a concrete mix would be small and would be limited in quantity. Where, on the other hand, the hardened concrete is continuously exposed to an aggressive water, the amount of aggressive agent is unlimited in quantity, and, particularly at the water-line, may build up concentrations in the concrete pores very much higher than that of the original water.

It would appear that a wide range of waters must be considered suitable for concrete making, and it can be assumed that any water which is suitable for drinking can generally be used for the manufacture of concrete. An exception is when the water contains sugar, for example, the waters of some Natal Coast rivers.

Where however, the water is obtained from a source that has not previously been proved satisfactory, specifications commonly require that at the age of 28 days, mortar made with ordinary portland cement and the particular water to be used shall have a compressive strength at least 85 per cent of that of mortar made with the same cement and water of known suitability.<sup>5</sup>

In an Appendix to B.S. 3148: 1958, Tests for Water for Making Concrete, it is suggested that the water may be considered suitable for making concrete if

(a) the initial setting time of a test specimen made with the suspect water does not differ from that of a control specimen made with distilled water by more than 30 minutes, and (b) the average 28-day strength of concrete test cubes made with the water is not less than 80 per cent of the corresponding strength of control cubes made with distilled water.

Professor Abrams, on the other hand, considered that a reduction of 15 per cent in the 28-day mortar strength should be the rigid maximum permitted, and that waters giving greater reductions should be regarded as unusable.

The 80 per cent strength criterion appears to be somewhat low and the Portland Cement Institute has adopted the 85 per cent limit suggested by Abrams.

It is known that the action of aggressive agents may only be detrimental over a long period of time, and it would therefore be unwise to rely entirely on a comparison of mortar or concrete strengths at early ages in the choice of a mixing water.

In the case of all waters from unproved sources it would seem a wise precaution to analyse the water before coming to any decision. Unfortunately, the interpretation of the results of such analyses is not easy. No standard limits have been set for the permissible amounts of deleterious materials, and indeed very little systematic research work has been done on this important aspect of concrete manufacture. All that can at present be attempted is to collate the isolated results from various experiments.

### CLASSIFICATION OF NATURAL WATERS

In South Africa we are fortunate in having available a comprehensive survey of the country's water resources.<sup>3</sup>

Dr. Bond classified the waters of the Republic as fol-

(1) **Pure Water Group.**—Waters containing dissolved solids not exceeding 150 mg/ $\ell$  with an average of 40 to 100 mg/ $\ell$ . Such waters are generally slightly acid, the amber waters of the Cape Province having a pH as low as 4,5.

Such pure waters occur in a large area of Natal (excluding Zululand and the coastal areas), Swaziland and the south-eastern Transvaal.

The water from boreholes and springs in the Magaliesberg quartzites of the central Transvaal and in the Waterberg, and sandstones of the north-western Transvaal belong to this Group.

(2) Carbonate Waters.—(a) Temporarily Hard Carbonate Waters.—In these, the total solids rarely exceed 600 mg/ $\ell$ . The pH varies from 7,5 to 8,0. They contain practically nothing but calcium and magnesium bicarbonates with little or no chlorides or sulphates.

A large area of the central and western Transvaal has water of this type.

(b) ALKALINE SODIUM CARBONATE WATERS.—In these waters the total salts rarely exceed 800 mg/ $\ell$ . They

contain, in addition to calcium and magnesium bicarbonates, appreciable sodium carbonate or bicarbonate (generally the latter). The pH is high and occasionally exceeds 8.8.

At least a third of the Republic has water of this alkaline type, particularly the central Free State, Lesotho, Eastern Province (excluding the coastal areas), western Natal and eastern and northern Transvaal (excluding the Zoutpansberg).

(3) Highly Mineralized Chloride-sulphate Waters. —In these waters the total dissolved solid content is usually over 1 000 mg/ $\ell$ , and in the arid north-west Cape occasionally approximates 10 000 mg/ $\ell$ . Usually the dissolved solid content varies from 1 000 to 4 000 mg/ $\ell$ , and the pH is usually about 7,0. These waters contain abundant chlorides and sulphates, and the hardness is mainly permanent.

At least half of the waters of the Republic are of this brackish type. They are mainly confined to the arid western half of the Republic, including however, the fairly well-watered coastal areas of the Cape Province. Saline waters are also found in the north-western Transvaal (Zoutpansberg and Letaba) and along the very well-watered Zululand coast.<sup>4</sup>

A study of the different classes of water would seem to result only in the broad generalization that nearly all our natural waters are suitable for concrete work, the exceptions comprising the more acidic water of Group (1) and some concentrated waters of Group (3). Moreover, any of the waters classified may be changed by pollution with waste waters, by mingling with sea-water, by passing over or through ground containing soluble salts or organic matter, or by any of a multitude of diverse agencies of contamination.

As the engineer is concerned only with the particular water which he intends using, it would be profitable to consider the effect of various dissolved salts and contaminating matter on the fresh concrete.

## COMMON IMPURITIES

The effects of some of the more common impurities in mixing water may be summarized as follows:

(a) **Sulphates.**—Abrams showed that sulphates in the mixing water produce no ill effects until an  $SO_4$  concentration of about 10 000 mg/ $\ell$  is reached. In this concentration the reduction in 28-day compressive strength is 10 per cent, while a concentration of 5 000 mg/ $\ell$  results in a loss of strength of 4 per cent. Water containing 28 000 mg/ $\ell$  of  $SO_4$  mainly in the form of magnesium sulphate produced a reduction in strength of 16 per cent, while a water containing 1 500 mg/ $\ell$  of sodium sulphate and the same quantity of sodium chloride produced no reduction in strength.

The results of a series of tests on the effect of distilled water containing dissolved salts have been reported by Singleton-Green. Mortar specimens were made up with samples of water containing 0, 5 000, 10 000, 20 000, and 40 000 mg/l respectively of the negative ion of each of the following salts: sodium chloride, sodium sulphate, sodium carbonate, magnesium chloride, calcium chloride, magnesium sulphate and ferrous sulphate.

It was found that "all the sodium salts used were injurious to portland cement mortars; equivalent ion concentrations of the chloride, sulphate and carbonate causing progressively greater reductions in strength". The two magnesium salts exercised little effect, while calcium chloride and ferrous sulphate were beneficial. A concentration of 20 000 mg/ $\ell$  of the sulphate ion in the latter case produced an increase of 20 per cent in the 28-day strength. It would appear that presence of excess sulphate is not

in itself sufficient grounds for the rejection of a mixing water, the type of sulphate having an important bearing on the harmful effect of the salt. This consideration is taken into account in the Spanish regulations for the design and construction of public works which require that the maximum amount of sulphuric anhydride must not exceed 3 000 mg/ $\ell$ ; while sulphides are limited to 5 000 mg/ $\ell$ . (b) Chlorides.—In the tests conducted by Abrams, solutions of common salt of concentrations below 10 000 mg/l produced a slight increase in strength at three and seven days. At later ages all solutions gave a substantial strength reduction. Strength reductions of 40 per cent were produced by solutions containing 200 000 mg/l at early ages, and by solutions of half that concentration at later ages. Solutions containing 50 000 mg/l reduced the strength by about 30 per cent.

Kleinlogel<sup>8</sup> suggests that a concentration of 30 000 mg/l of common salt be regarded as the limit for concrete mixing water. Presumably this is for plain concrete work.

For reinforced concrete work the presence of chloride may lead to corrosion of the reinforcing, and on this account it may be advisable to follow the Spanish regulations for public works, which restrict the amount of sodium or magnesium chloride to 10 000 mg/l in water for reinforced concrete. In all cases, however, the maximum percentages of chloride in concrete laid down in the Draft S.A.B.S. Specification for Concrete Work, <sup>17</sup> as set out in Table 4.I should be taken as the maximum permissible limits.

(c) Carbonates and Bicarbonates.—In a review of experimental data, Steinour<sup>14</sup> suggests that a limit of 2 000 mg/l of sodium carbonate or of sodium bicarbonate or of the sum of the two is generally tolerable. It is evident from the results of tests that these salts have different effects with different portland cements. Some investigators have

found that concentrations of sodium bicarbonate of up to 1,77 per cent of the cement mass reduced the strength of mortar cubes by only 15 per cent whereas others have reported that one per cent of either sodium carbonate or bicarbonate reduced the strength to 65 per cent of that of the controls. Steinour concludes that, although 2 000 mg/l may generally be safe, it is advisable to undertake tests both on strength and on setting time whenever the sum of the alkali bicarbonate and carbonate exceeds 1 000 mg/l.

The solubility of calcium and magnesium carbonates is low, and their effects in mixing water can consequently be disregarded. It is also known that the bicarbonates of calcium and magnesium are not harmful to concrete. (6, 8) (d) **Sea-water.**—As shown by the following analysis prepared by the U.S. Geological Survey, the average sea-

water contains mainly sodium and magnesium chloride and

•	m	ig/l
NaCl	. 27	100
$MgCl_2$	. 3	800
$MgSO_4$	. 1	650
CaSO <sub>4</sub>	. 1	260
$K_2SO_4$		860
MgBr <sub>2</sub>		80
CaCO <sub>3</sub>		120
Total	34	900

sulphates.

The experience and recommendations of a large number of authorities in connection with its use are conflicting, some reporting adverse results while others report no harmful effects.

It is probable that the diversity of opinion is due to differences in curing conditions and in ages of testing. Results of tests are of considerable interest since they give an indication of the effects of chlorides and sulphates, which may be found in other waters, on the strength and durability of concrete.

Abrams found that average sea-water which contains about 35 000 mg/l of salts, produced strength reductions at 28 days and over of 12 to 20 per cent for concretes cured in a moist room; but when air-cured, although the strength was lower for ages up to 3 months, at later ages the strengths were the same as for fresh-water concrete.

All authorities agree that in the present state of our knowledge it is inadvisable to use sea-water for reinforced concrete work.

(e) Carbon Dioxide.—Carbon dioxide has been used for the curing of concrete products on account of its effectiveness in reducing ultimate shrinkage. Exposure to excessive CO<sub>2</sub> at very early ages may result in the concrete surface becoming soft and chalky.<sup>13</sup>

Type of Concrete	Mass concrete  Efflorescence acceptable	Reinforced and post-tensioned concrete			Prestressed concrete (Pre-tensioned)		
Appearance or environmental conditions		Efflorescence not aesthe- tically desirable	Exposed to marine environ- ment	Not subject to marine exposure	Stressing strands and wires less than 5 mm in diameter	Wires over 5 mm in diameter	
Maximum chloride (Cl <sup>-</sup> ) content of concrete by mass of cement	2,0%	0,30%	0,20%	0,60%	0,05%	0,08%	

Note (i) Where different types of concrete are being placed on a site, the chloride content of the materials (water plus aggregate) shall not exceed that applicable to the most critical application.
(ii) The chloride contents (CI<sup>-</sup> by mass) of some common salts may be assumed to be:

NaCl: 61%; CaCl2: 64%; MgCl2: 74%.

Very pure waters containing free carbon dioxide corrode hardened concrete. However the amount of free carbon dioxide which can be present in the limited proportion of water used in making concrete is so small that its deleterious effect is negligible.

- (f) Waste Waters.—In his experiments, Abrams found that:
  - (i) Brewery and soap works wastes produced no reduction in concrete strengths.
  - (ii) Tannery wastes generally produced strength reductions, the highest reduction being 20 per cent.
- (iii) A river water highly polluted with stockyard wastes produced no reduction in strength.
- (iv) Water containing sanitary sewage gave essentially the same strength as fresh water. River water containing a considerable quantity of sewage showed reductions of 16 per cent for moist-cured concrete, but a maximum of 8 per cent for air-cured concrete.
- (v) Waste water from a paint factory gave strength reductions of 10 to 20 per cent.

Kleinlogel8 states that:

- (vi) Waste water from coke plants should not be used.
- (vii) Waste water containing lactic acid, tannic acid, fruit juices, alcohol, sugar, chlorine (from paper works), fertilizer or in general any organic or other acid or carbohydrate should be regarded as dangerous until tested and proved satisfactory.
- (g) Waters Containing Inorganic Acid.—Some colliery and mine waters contain fairly high percentages of sulphuric acid resulting from the oxidation of pyrites or other sulphides. Abrams tested waters containing as much as 6 250 mg/l of sulphuric acid and found the strengths to be about 85 per cent of that of the controls. Other tests<sup>15</sup> have shown that with mixing water containing 8 600 mg/l of total acidity the strength was generally better than that of the controls.

Tests on mixing water containing hydrochloric acid in a concentration of over 10 000 mg/ $\ell$  resulted in no impairment either of setting time or of strength.14

(h) Marsh Waters.—Abrams found that a number of bog waters, which were generally thought to be unsuitable for concrete making, contained only small quantities of foreign materials and gave good results in concrete, the strength reduction seldom being greater than 10 per cent.

In this connection Bond has pointed out4 that the brown waters of the Table Mountain Series of the Cape Province rarely contain organic matter in quantities exceeding 30 mg/l, so that their humic acid content would be of negligible effect in concrete.

On the other hand, it has been reported by Singleton-Green<sup>6</sup> that quantities of humic acid as low as 780 mg/l seriously affected the strength of the concrete and retarded the set.

Experiments undertaken by Grün<sup>9</sup> indicate that a humic acid content of one per cent by mass of the sand constituent of mortar completely inhibited the setting of cement. It should be pointed out that this amount of acid is equivalent to a concentration of about 110 000 mg/l in the mixing water, which is far in excess of that contained in natural waters.

Humic and other organic acids have been successfully neutralized by allowing the water to percolate through beds of loose limestone or marble chips.

The Spanish public works regulations specify a maximum of 3 000 mg/l of organic material in the mixing water, which appears to allow a very reasonable latitude in this respect.

(i) Water Containing Algae.—A number of tests on the effects of algae in the mixing water have been reported by Doell. 12 It would appear that the presence of algae results in the entrainment of air in the mix, 0,1 per cent algae by mass of mixing water entraining 6 to 7 per cent of air. The test mixes were therefore regarded as mixes containing air-entraining admixtures, and were designed accordingly, adjustments being made to suit the amount of air entrained.

It was found that, providing suitable modifications were

made in the mix proportions, the presence of 0,075 per cent of algae did not reduce the strength of concrete by more than 15 per cent, which is considered an allowable reduction. The presence of 0,1 per cent algae caused a strength reduction of more than 15 per cent, and on that account must be regarded as exceeding the permissible limit

(j) Miscellaneous Inorganic Impurities.—In a review of a survey carried out by Kuhl on the effects of miscellaneous inorganic salts on the strength of cement paste Steinour<sup>14</sup> reports:

These tests were made with just one portland cement and just one amount of salt (the chemical equivalent of two per cent of calcium chloride by mass of cement).

The salts chosen constituted a cation series and an anion series. For the cation series, chlorides were used except where solubility was low, in which case nitrate was used.

Cations tested were:

lithium ammonium barium sodium magnesium copper potassium calcium zinc cadmium iron cobalt aluminium manganese tin chromium nickel lead

The salts of the cation series that caused a significant reduction in strength were those of:

manganese tin zinc copper lead (nitrate)

In general, quantitative data were not given but the discussion reads in terms of both tensile and compressive strengths, determined at early ages. Of the five salts listed, the last three were the most active. The zinc and copper chlorides retarded so greatly that no strength tests could be made at two and three days, but active hardening then began, and 7 and 28-day strengths were about normal. The action of the lead of the lead nitrate was said to be completely destructive.

The anion series comprised sodium salts of the following:

fluoride chlorate hydrosulfite chloride perchlorate thiosulfate bromide iodate sulfite iodide silicofluoride sulfate nitrate phosphate nitrite arsenate chromate borate bichromate aluminate

Of these salts, the only ones that reduced the strength markedly were:

sodium iodate sodium phosphate sodium arsenate sodium borate

These were said to reduce the initial strength to an extraordinarily great degree, and in certain instances to zero.

Salts that produced no pronounced detrimental effect at the relatively high concentrations that were tested may be presumed to be relatively safe in the smaller concentrations such as might be encountered in industrially contaminated mix water.

It is probable that some of the agents that Kuhl found to give satisfactory strengths nevertheless have pronounced effects on setting times. Some of them have reputations as retarders or accelerators, and indeed almost any compound at such high concentration might have some effect on setting. The effects would in general be less at the smaller concentrations such as might be encountered in practice. Nevertheless, it seems worth while to emphasize again the desirability of making simple setting tests with unknown waters carrying dissolved solids unusual in nature or amount, even though the amount may not seem excessive.

(k) Water Contaminated by Oil.—Generally oil contamination can be removed by flotation. Nevertheless, tests carried out by Davis<sup>16</sup> are of considerable interest.

The tests were carried out on structural grade concrete made with 20 mm Reef quartzite stone, and a Reef quartzite crusher sand. The oil was added initially to the dry aggregates and cement before the addition of water. The amount of oil added was expressed in terms of percentage oil by mass of cement. 2%, 4% and 8% oil were added. As a guide it may be pointed out that for normal structural grade concrete 2% oil by mass of cement is roughly equivalent to ¾% by mass of sand and ½% by mass of stone. Three different oils were added—a mineral oil as used for car lubrication (SAE 30), a diesel fuel oil and a vegetable seed oil (sunflower). A control mix with no oil was used as a standard of comparison.

In all the mixes water was added to achieve a standard workability which, in this case, was 50 mm slump. In general, all the oils had a lubricating effect on the fresh concrete which made it possible to reduce the water content of the mix while still achieving the same workability as that of the control mix. The consequent increase in cement: water ratio would therefore be expected to produce strengths higher than those given by the control mix.

All the specimens were stripped at 24 hours and all except those tested at 24 hours were cured in water until the time of test.

Davis16 summarised the results as follows:

2% by mass of *mineral oil* resulted in significant increases in strength at all ages. Increases of approximately 65% at early ages were recorded. At three months the increase in compressive strength was about 35%. Addition

of 4% and 8% of mineral oil also resulted in strength gains but these were not as large as those resulting from 2% addition.

The addition of 2% by mass of diesel oil resulted in increases in compressive strength at all ages. With 4% of oil, minor strength increases were observed at ages between seven days and three months. The addition of 8% of oil slightly reduced the strength of the concrete.

The addition of 2% and 4% of sunflower oil resulted in slight increases in compressive strength at all ages. The addition of 8% of oil had a detrimental effect on the concrete, particularly at later ages when the strength reductions were about 30%.

## PRACTICAL CONSIDERATIONS

When undertaking important concrete work it should be remembered that not only must the analyst's report on the water be interpreted, but the water actually used should be of a quality at least as high as that of the sample analysed.

Before undertaking the analysis the chemist generally allows all sediment to settle, removes all scum and floating debris, and then analyses the clear supernatant water.

When using the water on the job, the engineer should in the same way remove all debris and allow for the settlement of sediment. Moreover, the possibility of contamination by flood waters and of concentration by evaporation must be avoided.

In this connection it is recommended that when drawing off from a lake or stream, a no-fines weir should be built above the draw-off point to a level above highest expected flood-water and the water to be used for mixing allowed to percolate through the weir into a settlement basin or channel.

While the above discussion may provide valuable guide-lines, nevertheless an over-riding criterion is that the strength of concrete or mortar cubes should be not less than 85 per cent of that of corresponding cubes made with the same cement and aggregates and water from a proved source.

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