# TOXICITY OF PORTLAND CEMENT

# TO SALMONID FISH

PREPARED FOR:

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APRIL 1983

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## SUMMARY

## TOXICITY OF PORTLAND CEMENT TO SALMONID FISH

1. Controlled laboratory bioassays using young rainbow trout were conducted to determine if Portland cement (the active ingredient of raw concrete) mixed with freshwater is toxic to salmonid fish.

2. All strengths of cement tested (100 $mg \cdot L^{-1}$ or higher), when mixed with Wakefield Creek or Vancouver City dechlorinated tap water, killed fish and caused an appreciable elevation of the pH of these waters.

3. Cement:freshwater mixtures with pH values elevated to 10.5 or higher were toxic to fish within 20 - 50 minutes; whereas more dilute strengths (initial pH values 9.7 - 9.8) killed 60% of the test fish within the 24-hour test period. All control fish, held in Wakefield Creek or Vancouver City tap water without cement added, survived this 24-hour test period and appeared normal.

4. Based on these findings and on a review of available information concerning the toxicity of high pH to salmonid fish in freshwater, it was concluded that the reported fish kill in Wakefield Creek during the morning of August 7, 1981 was most likely caused by the spillage of raw concrete into the creek on this occasion.

# TOXICITY OF PORTLAND CEMENT TO SALMONID FISH

## INTRODUCTION

### OBJECTIVES

To determine if Portland cement, when mixed with Wakefield Creek or other freshwater, is toxic to juvenile salmonid fish.

To examine pH and times to death of fish held in a range of concentrations of Portland cement in Wakefield Creek or Vancouver City water.

To assess these findings in conjunction with those specific to the deposition of raw concrete in Wakefield Creek on August 7, 1981.

### BACKGROUND

During the morning of August 7, 1981, the B.C. Ministry of Highways and Transportation spilled raw concrete into Wakefield Creek at the Highway 101 crossing (3.2 km north of Sechelt, B.C.) (1,2). At 1100 h, dead and dying fish (salmonids, sculpins) were observed in this creek, immediately downstream of the culvert pipe where concrete was being poured into baffles, by Federal Fisheries Officer R.B. Tancock and Conservation Officer J. A. Stephen Jr. The creekwater was turbid grey downstream of the culvert pipe, and clear upstream. Samples of creekwater were taken by Mr. Tancock at this time, at points 0.3 metres upstream of the culvert entrance and 1.2 metres downstream of the culvert outflow (1). Samples of dead fish and creekbottom sludge were also collected downstream of the culvert (1). Subsequent chemical analyses of the creekwater samples by Environment Canada laboratory technician Mrs. M. Grewal (3) indicated a pH value of 7.6 for the upstream creek water, and pH 11.9 for the downstream sample.

Criminal charges have since been laid (Crown vs. B.C. Ministry of Highways and Transportation) under Section 33 of the Federal Fisheries Act.

In order to provide ancillary technical information pertinent to the above, controlled laboratory bioassays were conducted with Portland cement (the active ingredient of raw concrete) and rainbow trout. Groups of fish were exposed to a range of concentrations of cement mixed in Wakefield Creek or Vancouver City water. The pH of each mixture was measured at the beginning and end of the test period (24 h or at time of death of the last fish in each mixture). Additionally, the times to death of fish in each mixture were recorded. Findings from these bioassays are presented and considered in this report.

## MATERIALS AND METHODS

### SAMPLE DETAILS

A 40 kg bag of normal Portland cement (Genstar, CSA type 10) was purchased from a local retail store on April 4, 1983. This unopened bag of cement was kept locked and in the personal possession of D. McLeay until April 11, when it was transported to the laboratory facility of D. McLeay & Associates Ltd. at B.C. Research (Vancouver, B.C.). The bag was inspected at this time and found to be tightly sealed.

An 80-litre sample of Wakefield Creek water was received at B.C. Research by D. McLeay from R.B. Tancock on April 11, 1983 at 1200 h. This sample was contained in four 20-litre clear plastic jerricans. Each jerrican was filled completely, sealed (sealing wax) and scribed as follows: "RBT 83/4/10 2:00 P.M. Wakefield Creek." Two 1-litre glass jars were also received from Mr. Tancock on this occasion for chemical analyses. Each jar was sealed and scribed "RBT 83/4/10 Wakefield Cr. 2:15 P.M."

On April 11 at 1630 h, a 2-litre sample of Vancouver City dechlorinated tap water was taken from the treated water supply at the bioassay facility, and placed in two 1-litre new plastic bottles. Each bottle and cap were rinsed thoroughly three times with this water, before filling and sealing (4). Each of these bottles was scribed "D McL 11/4/83 Vanc. City dechlor. tap water (B.C. Research)." This sample and the two 1-litre bottles of Wakefield Creek water were kept in the possession of D. McLeay until the morning of April 12, whereupon they were taken to West Vancouver and given to Mr. R. Holowaty (Chemist, Laboratory Services Quality Control, Environment Canada). Each of these two water samples was analysed for the following: pH, conductance, alkalinity, EDTA hardness, and nonfiltrable residue (suspended solids) (4).

The samples of Wakefield Creek water and Portland cement were locked in the bioassay room (air temperature 15 ± 1° C) overnight.

## TEST FISH

Young fingerling rainbow trout (<u>Salmo gairdneri</u>) were used as test fish. These fish were obtained as eyed eggs from the Mount Lassen Trout Farms hatchery (Red Bluff, California); and were fully acclimated to Vancouver City dechlorinated tap water prior to bioassays. Fish were fed an excess ration of Oregon Moist Mash, 6 - 8 times daily, and were not fed during the day that bioassays were conducted. All fish appeared healthy and were actively feeding for several days prior to these tests. Mortalities in the rearing trough were negligible.

These fish were reared outdoors under natural daylight conditions. Fish size measured at the time of the bioassay tests was as follows (mean values, with range in parentheses):

| | |
|---|---|
| Length (cm): | 3.6 (3.1 - 4.3) |
| Weight (g): | 0.48 (0.29 - 0.79) |
| Condition factor ($kW \cdot L^{-3}$) | 1.0 (0.9 - 1.1) |

## TEST DETAILS

Basic procedures for these bioassay tests with Portland cement were according to "Provincial Guidelines and Laboratory Procedures for Measuring Acute Lethal Toxicity of Liquid Effluents to Fish" (5) and "Standard Methods" (4).

On April 11, 1983, 20-litre volumes of Wakefield Creek water (temperature, 15°C) were transferred from sealed containers to each of four recycle test tanks (Fig. 1). Identical volumes of Vancouver City dechlorinated tap water (15°C) were added to each of six additional recycle tanks. The water in each tank was recirculated (and aerated) by a pump, at a rate of 10 litres·$min^{-1}$. Supplemental aeration was not required. These tanks were designed according to Provincial recommendations for evaluating the toxicity to fish of water or effluent containing high levels of settleable solids (5).

Each bioassay tank was housed within a controlled temperature (15 ± 1°C) room. Lighting was overhead incandescent illumination, regulated by time clock and automated on/off dimmer control to provide a 14 h light: 10-h dark cycle, with a 30-minute period ("dawn", "dusk") of varying intensity.

Ten fish were introduced randomly to each test tank. These fish were observed for a minimum of 30 minutes prior to the addition of cement, in order to ensure that no deaths were caused by netting and transfer. Thereafter, pre-weighed amounts of Portland cement were mixed and introduced gradually (2-minute interval) to each of eight tanks until the desired test strengths (Table 1) were attained. The remaining two tanks, containing Wakefield Creek or Vancouver City dechlorinated tap water only, served as freshwater controls.

The initial (starting) pH of each cement:freshwater mixture was measured, and the time to death of each fish recorded. The final pH (at death of last fish; or at 24 h if surviving fish) of each mixture was also determined. pH values were measured using a Metrohm Herisan Model E488 portable pH meter, calibrated and checked periodically with pH 7.0 and 10.0 buffers.

The initial and final temperature and dissolved oxygen content of each test mixture were measured. Dissolved oxygen content was determined using a Delta Scientific Ltd. Model 1010 portable dissolved oxygen meter.

Each bioassay was terminated upon the death of the last fish, or at 24 h (1440 minutes) for surviving fish.

## REVIEW OF TECHNICAL LITERATURE

The technical literature was searched for published information concerning the toxicity of concrete or high pH to fish. Review articles "Effects of pollution on freshwater fish" published yearly by the Water Pollution Control Federation Journal were searched manually (1977 - 1982 incl.). Additionally, a computer search was conducted. Key words employed were: toxicity, lethal, sublethal, fish, salmonid, Portland cement, building cement, construction cement, concrete, high pH, and alkaline pH.

The following data bases were consulted:

| | |
|---|---|
| Biological Abstracts | 1967-1983 |
| Chemical Abstracts | 1972-1983 |
| ELIAS | 1976-1982 |
| Excerpta Medica | 1975-1979 |
| NTIS | 1964-1983 |
| Pollution Abstracts | 1970-1983 |

## RESULTS

The fish bioassay results for differing strengths of Portland cement in Wakefield Creek or Vancouver City are given in Table 1. For rainbow trout exposed to cement concentrations of 1000 and 500 $mg \cdot L^{-1}$ (parts per million) in Wakefield Creek water, times to death of 50% of the test fish (LT50 values) were 29 and 45 minutes, respectively. The lowest strength of cement mixed in this creekwater (100 $mg \cdot L^{-1}$) killed six of the ten test fish within 24 hours; whereas all fish held in Wakefield Creek water alone (no cement added) were alive and appeared normal at the termination of the test period.

Bioassay results for cement:Vancouver City water mixtures were similar. The highest cement strength tested (5000 mg·L$^{-1}$) killed all fish in less than 20 minutes; and LT50 values for concentrations as low as 300 mg·L$^{-1}$ were 68 minutes or less (Table 1). Times to death of fish decreased progressively with increasing concentrations of cement in freshwater. The 40% survival of fish held for 24 h in the lowest strength examined (100 mg·L$^{-1}$) was identical to that found for this concentration when diluted with Wakefield Creek water. As with this creekwater sample, all control fish held in Vancouver City water without the presence of cement survived the 24-h test period.

Although fish behaviour was not studied in detail during these bioassays, dying fish were observed swimming at the surface of each cement:freshwater mixture. Loss of fish equilibrium was evident. Body epithelium became discolored (dark patches) prior to or at time of death of these fish.

All strengths of Portland cement mixed with Wakefield Creek water caused an elevation of pH values from that determined for the uncontaminated creekwater (Table 1). The pH values for cement strengths of 500 and 1000 mg·L$^{-1}$ in Wakefield Creek water were 10.5 - 10.7 (Table 1); these values did not change appreciably during the bioassays. The pH for the lowest strength of cement mixed with this creek water declined from an initial value of 9.8 to 9.0 during the 24-hour test period. The pH of Wakefield Creek water without cement added (control) was near neutrality (6.6 - 6.7).

As with the cement:Wakefield Creek mixtures, all mixtures of cement in Vancouver City water showed a progressive increase in pH values with increasing cement concentrations. For each diluent water type, the pH of all strengths of Portland cement which killed these salmonid fish in 95 minutes or less was consistently elevated to values of 10.2 or higher (Table 1). The pH value for the lowest strength of cement tested in Vancouver City water (100 mg·L$^{-1}$) declined from an initial value of 9.7 to 8.9 at 24 h. Vancouver City water without cement added remained at pH 6.4 - 6.5 throughout this test period.

The water temperature of each cement:freshwater mixture remained at 15 ± 1°C during the bioassay tests. Dissolved oxygen content of each mixture was 90% saturation or greater ($\geq$ 9 mg $O_2 \cdot L^{-1}$) throughout the test period.

The chemical analytical values determined for each of the two freshwater sources used as diluent/control waters in these bioassay tests are presented in Table 2. All values derived for the sample of Vancouver City dechlorinated tap water are typical of previous analyses of this water source. The pH, conductance, alkalinity and hardness values for the sample of Wakefield Creek water were somewhat higher than respective values for Vancouver City water; although these values are consistent with B.C. coastal streamwater. Concentrations of suspended solids (nonfiltrable residue) were moderately low (Wakefield Creek water) or below the limit of detection for the analytical technique used (Vancouver City water) (Table 2).

## DISCUSSION

Findings from these controlled laboratory bioassays demonstrate conclusively that Portland cement, if mixed with Wakefield Creek or other soft freshwater sources, is acutely toxic to salmonid fish. Although no published information was uncovered concerning the toxicity of Portland cement, uncured concrete has previously been shown to be toxic to fish. In its report on the hazards of extreme pH values to freshwater fish (6), the European Inland Fisheries Advisory Commission cited an earlier (1936) study by H.J. Bandt which found that concrete blocks acted as a source of alkali (high pH) in water, resulting in deaths of trout at pH values of 9.2 and higher. This finding is consistent with the present studies with Portland cement.

The principal ingredient of Portland cement is limestone ($CaCO_3$) and a clay material containing silica ($SiO_2$), alumina ($Al_2O_3$), ferric oxide ($Fe_2O_3$) and minor components (ie. MgO). A typical Portland cement may indicate on analysis: lime 64%; alumina 5.5%; ferric oxide 3%; silica 22%; sulphur trioxide 2%; and magnesia 1.5% (7). Raw concrete is formed by mixing appropriate quantities of Portland cement, silica sand and gravel. Chemical additives may also be included to promote quick curing.

The toxicity of Portland cement (or of raw concrete) to fish, if added to fresh water, is attributed primarily to the high (alkaline) pH produced upon hydrolysis of limestone ($CaCO_3$) to calcium hydroxide, $Ca(OH)_2$. Addition of calcium hydroxide, sodium carbonate ($Na_2CO_3$) or sodium hydroxide (NaOH) to fresh water has been shown to cause fish deaths within a matter of minutes or longer (depending on concentration); this toxic effect is thought to be due to the alkaline pH caused by the hydroxyl ($OH^-$) ions (6). Other ingredients of Portland cement (quick-curing additives, alumina) may also contribute to its toxicity to fish. Low concentrations of aluminum, if dissolved in water, can kill fish within minutes; and the solubility of this metal is increased at pH values above 8.0 (8,9).

Field investigations have reported fish kills in freshwater streams or lakes, caused by alkaline pH. Eicher (10) noted that rainbow trout stocked into lakes receiving runoff water flowing over limestone formations were killed when the pH values rose to 9.6 or higher. Other researchers found major fish kills in a river following the accidental entry of an alkaline fly ash slurry (11).

Although the effects of alkaline pH on fish have not been examined extensively, a number of controlled laboratory studies have determined the acute lethal tolerance of salmonid fish to high pH. In general, freshwater solutions with a pH value greater than 10.0 are likely to be rapidly lethal to young salmonid fish (6,12-15). Freshwater with pH values of 9.0 to 10.0 have also been reported to cause deaths of salmonid fish (12,13,16). Witschi and Ziebell (16) reported reduced survival of hatchery-reared rainbow trout, 20-25 cm in length, held for 24 h in soft freshwater adjusted to pH 9.5 with sodium hydroxide.

Neither fish size nor water temperature (within the range 10 - 20°C) appear to alter the short-term tolerance of salmonids to high pH[13]. Destruction of fish gill and skin epithelial tissues due to these alkaline pH values are believed to be the cause of the deaths observed (6).

The above findings for reduced lethal tolerance of salmonid fish due to high pH waters are consistent with those shown in this report to be caused by Portland cement.

A number of sublethal toxic effects on salmonid fish have been reported to be caused by elevated pH levels in fresh water. Witschi and Ziebell (16) reported sluggish behaviour or loss of equilibrium for juvenile rainbow trout subjected to pH values of 9.0 or higher. These authors also noted a reduction of feeding activity at pH 9.0 (16). Hargis (17) found that young rainbow trout held in pH 9.0 water for 30 minutes or longer displayed an elevated oxygen consumption rate and a greater frequency of coughs, when compared with fish held in freshwater at pH 7 or 8. Daye and Garside (18) reported gill histopathologies for brook trout (Salvelinus fontinalis) exposed to pH 9.0 water, with more extensive effects to gills and other tissues at pH 9.5. These authors have also shown (19) that pH values of 9.0 to 9.5 are deleterious to young Atlantic salmon (Salmo salar).

From the foregoing, it is apparent that freshwater with pH values elevated to 9.0 - 9.5 is likely to be harmful to resident salmonid fish, and that fish mortalities are imminent if the pH is increased beyond 10.0. This information, considered together with the rapid (within 20 - 50 minutes) deaths of fish held in Portland cement:freshwater mixtures with pH values of 10.5 or higher, and the pH value of 11.9 reported for the downstream sample of Wakefield Creek water sampled August 7, 1981 (3), suggest strongly that the dead fish found on this date in Wakefield Creek were killed by the observed spillage of raw concrete into the creek (1,2).

## REFERENCES


1. Tancock, R.B. 1981. Memo to file dated August 14, 1981.

2. Stephen, J.A. Jr. 1982. Memo to file dated January 11, 1982.

3. Grewal, H.K. 1981. Analytical sheet dated August 28, 1981 entitled "Sample No. 810514 - Legal samples from Wakefield Creek". Laboratory Services, Environment Canada.

4. Anon. 1980. Standard Methods for the Examination of Water and Wastewater. Fifteenth edition. American Public Health Association, Washington D.C. 1134 pp.

5. B.C. Ministry of Environment. 1982. Provincial Guidelines and Laboratory Procedures for Measuring Acute Lethal Toxicity of Liquid Efluents to Fish. November 1982. Victoria, B.C. 18 pp.

6. EIFAC 1969. Water quality criteria for European freshwater fish - extreme pH values and inland fisheries. Water Res. 3: 593-611.

7. VanThoor, T.J.W. 1971. Materials and Technology. Vol. II. Non-metallic ores, silicate industries, and solid mineral fuels. Longman - J.H. DeBussy, London. 828 pp.

8. Everhart, W.H. and R.A. Freeman. 1973. Effects of chemical variations in aquatic environments. Vol. III. Toxic effects of aqueous aluminum to rainbow trout. U.S. Environmental Portection Agency. Ecol. Res. Series EPA-R3-73-011b. February 1973. Washington, D.C. 41 pp.

9. Hunter, J.B., S.L. Ross and J. Tannahill. 1980. Aluminum pollution and fish toxicity. Wat. Poll. Control 79: 413-420.

10. Eicher, G.J. 1946. Lethal alkalinity for trout in waters of low salt content. J. Wildl. Manag. 10: 82-85.

11. Spehar, R.L. et al. 1979. Effects of pollution on freshwater fish. J. Water Poll. Control Fed. 51: 1616-1692.

12. Jordan, D.H.M. and R. Lloyd. 1964. The resistance of rainbow trout (Salmo gairdnerii Richardson) and roach (Rutilus rutilus L.) to alkaline solutions. Int. J. Air Wat. Poll. 8: 405-409.

13. Daye, P.G. and E.T. Garside. 1975. Lethal levels of pH for brook trout, Salvelinus fontinalis (Mitchill). Can. J. Zool. 53: 639-641.

14. McLeay, D.J. and C.C. Walden. 1976. Effect of pH on bioassays in fresh and seawater. CPAR Rep. 402. Can. For. Serv. Ottawa, Ont. 75 pp.

15. McLeay, D.J., C.C. Walden and J.R. Munro. 1979. Effect of pH on toxicity of kraft pulp and paper mill effluent to salmonid fish in fresh and seawater. Water Res. 13: 249-254.

16. Witschi, W.A. and C.D. Ziebell. 1979. Evaluation of pH shock on hatchery-reared rainbow trout. Progr. Fish-Cult. 41: 3-5.

17. Hargis, J.R. 1976. Ventilation and metabolic rate of young rainbow trout (Salmo gairdneri) exposed to sublethal environmental pH. J. Exp. Zool. 196: 39-44.

18. Daye, P.G. and E.T. Garside. 1976. Histopathologic changes in surficial tissues of brook trout, Salvelinus fontinalis (Mitchill), exposed to acute and chronic levels of pH. Can. J. Zool. 54: 2140-2155.

19. Daye, P.G. and E.T. Garside. 1980. Development, survival, and structural alterations of embryos and alevins of Atlantic salmon, Salmo salar L., continuously exposed to alkaline levels of pH, from fertilization. Can. J. Zool. 58: 369-377.

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TABLE 1

LT50 BIOASSAY RESULTS FOR RAINBOW TROUT[a]
EXPOSED TO PORTLAND CEMENT[b]

Wakefield Creek water received: April 11, 1983 Bioassays started: April 12, 1983

| Cement Concentration ($mg \cdot L^{-1}$) | Diluent Water | Initial pH | Final pH | % Survival of Fish | | | | LT50[c] (minutes) |
|---|---|---|---|---|---|---|---|---|
| | | | | 0.5h | 1h | 2h | 24h | |
| 1000 | Wakefield Creek[d] | 10.7 | 10.5 | 50 | 0 | 0 | 0 | 29 (23 - 40) |
| 500 | Wakefield Creek | 10.6 | 10.7 | 100 | 0 | 0 | 0 | 45 (33 - 51) |
| 100 | Wakefield Creek | 9.8 | 9.0 | 100 | 100 | 100 | 40 | <1020 (>60 - >1440) |
| 0 (control) | Wakefield Creek | 6.6 | 6.7 | 100 | 100 | 100 | 100 | - |
| 5000 | Vancouver City[e] | 11.3 | 11.3 | 0 | 0 | 0 | 0 | 16 (12 - 19) |
| 1000 | Vancouver City | 10.6 | 10.5 | 0 | 0 | 0 | 0 | 21 (18 - 28) |
| 500 | Vancouver City | 10.6 | 10.6 | 0 | 0 | 0 | 0 | 38 (30 - 45) |
| 300 | Vancouver City | 10.2 | 10.4 | 100 | 80 | 0 | 0 | 68 (55 - 95) |
| 100 | Vancouver City | 9.7 | 8.9 | 100 | 100 | 100 | 40 | <1095 (>135 - >144 |
| 0 (control) | Vancouver City | 6.4 | 6.5 | 100 | 100 | 100 | 100 | - |

[a] Mean weight, 0.48 g (range 0.29 - 0.79 g); mean length, 3.6 cm (range 3.1 - 4.3 cm).
[b] Genstar normal Portland cement, purchased April 4, 1983.
[c] Lethal time to death of 50% of test fish (range of times to death for 10 fish in parentheses).
[d] Received in sealed 20-L plastic jerricans from Fisheries Officer R.B. Tancock.
[e] Dechlorinated tap water.

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TABLE 2

CHEMICAL ANALYSES[a] OF SAMPLES OF WAKEFIELD CREEK AND VANCOUVER CITY DECHLORINATED TAP WATERS

| Constituent | Water Sample | |
|---|---|---|
| | April 10, 1983<br>Wakefield Creek | April 11, 1983<br>Vancouver tap |
| pH | 7.1 | 6.2 |
| conductance ($umho \cdot cm^{-1}$) | 55.3 | 17.0 |
| alkalinity ($mg\ CaCO_3 \cdot L^{-1}$) | 17.0 | 3.5 |
| hardness ($mg\ CaCO_3 \cdot L^{-1}$) | 18.0 | 5.0 |
| nonfiltrable residue ($mg \cdot L^{-1}$) | 13.5 | < 5.0 |

[a] Values determined by Mr. R. Holowaty (Laboratory Services Quality Control, Environment Canada, West Vancouver).