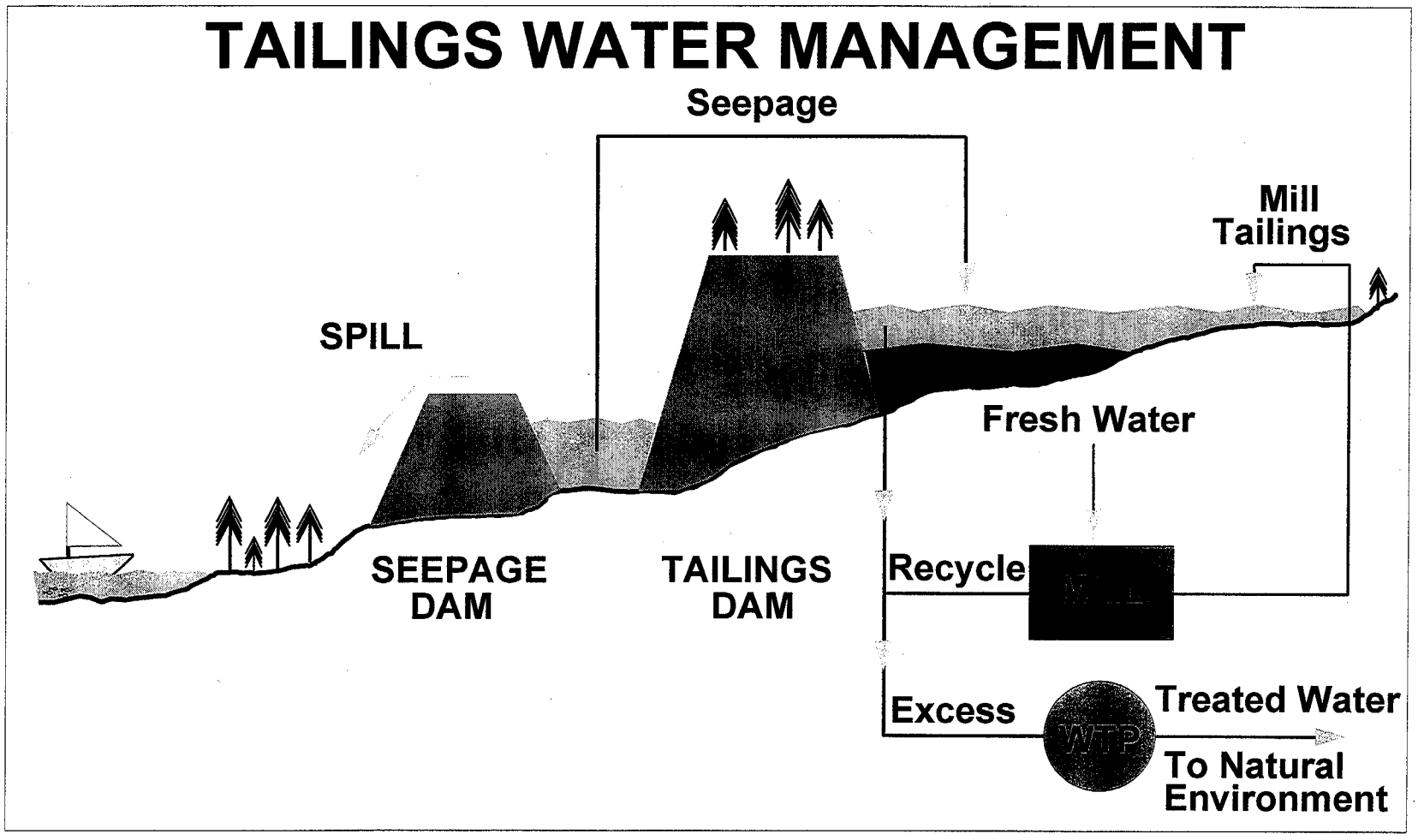
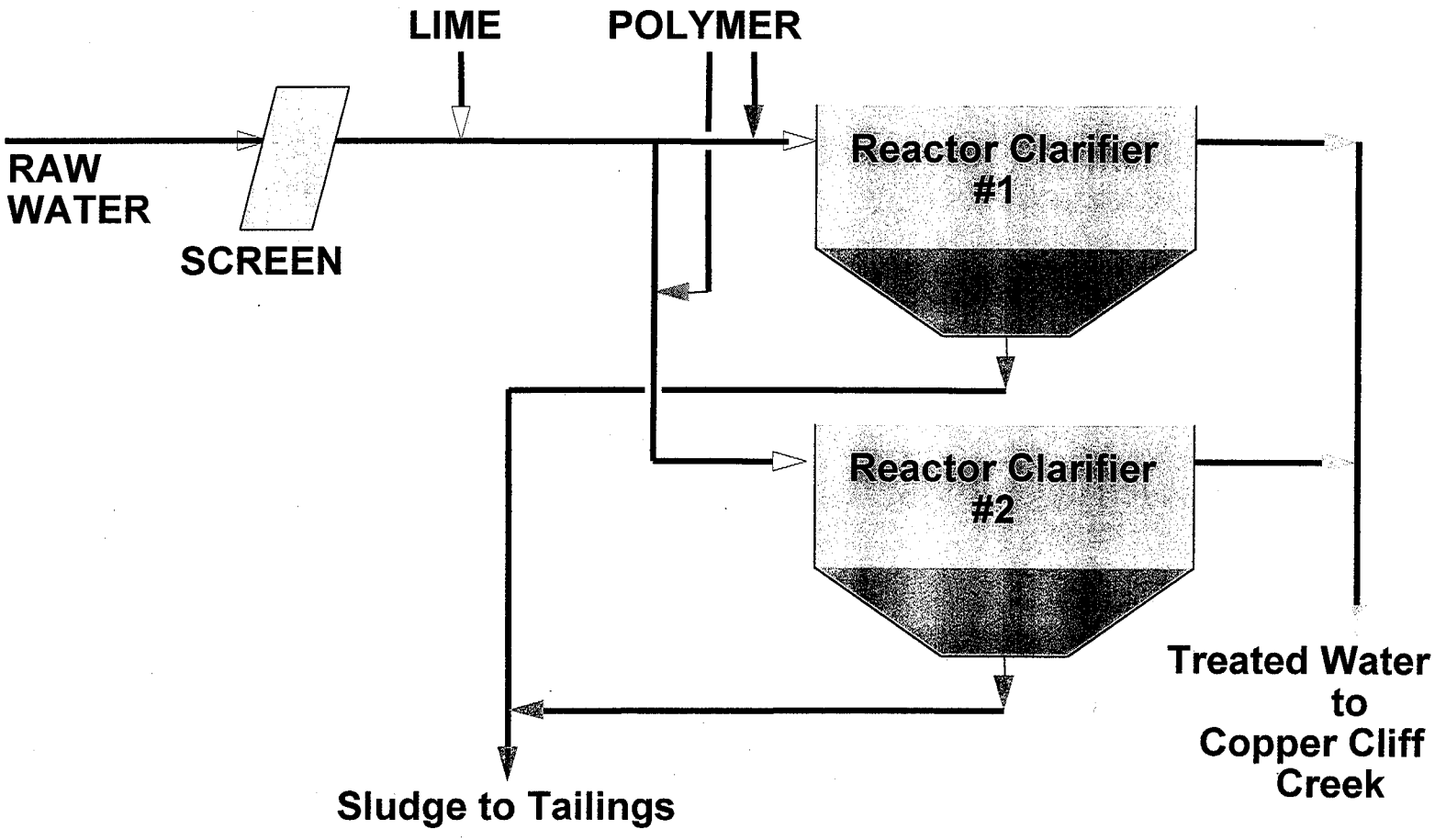
Copper Cliff Waste Water Treatment Plant

INCO

Glen Watson


TAILINGS WATER MANAGEMENT
Seepage
Mill Tailings
SPILL
Fresh Water
SEEPAGE DAM
TAILINGS DAM
Recycle
Excess
WTP
Treated Water
To Natural Environment

COPPER CLIFF CREEK WASTEWATER TREATMENT PLANT



Effluent Chemistry (typical values)

IN			OUT		
pH	**4.5**		pH	**11.0**	
NH_3N	**6.0**	mg/L	NH_3N	**6.0**	mg/L
Ca^{2+}	**100**	mg/L	Ca^{2+}	**300**	mg/L
Na^{+}	**100**	mg/L	Na^{+}	**100**	mg/L
K^{+}	**30**	mg/L	K^{+}	**30**	mg/L
Mg^{2+}	**80**	mg/L	Mg^{2+}	**80**	mg/L
Cl^{-}	**75**	mg/L	Cl^{-}	**75**	mg/L
SO_4^{2-}	**1200**	mg/L	SO_4^{2-}	**1200**	mg/L
NO^{3-}	**5.0**	mg/L	NO^{3-}	**5.0**	mg/L

Effluent Chemistry (typical values)

IN		OUT	
(total metal concentrations in mg/L)			
Fe	**30.0**	Fe	**0.30**
Mn	**1.0**	Mn	**0.02**
Ni	**10.0**	Ni	**0.25**
Cu	**1.2**	Cu	**0.05**
Zn	**0.10**	Zn	**0.01**
Al	**1.5**	Al	**0.15**
Co	**0.25**	Co	**0.01**

Environmental Concerns

- pH of effluent > 9.5 (MISA limit)
- Effluent frequently toxic to Rainbow Trout and *Daphnia magna* (> 50% mortality)
- Toxicity Identification Evaluations (TIE) determined that toxicity was possibly due to high ammonia and/or high metal concentrations.

Ammonia toxicity in alkaline effluent: The influence of atmospheric carbon dioxide on pH and un-ionized ammonia.

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4 main studies initiated between 1993 and 1997 to investigate the cause of toxicity

- The first two studies completed by consultants/commercial laboratories.
  - Modified Phase I TIE and Phase I TIE
- Next two studies completed by an M.Sc. Student and University professor (L.U.).
  - pH adjustment and treatability investigations

1993 Modified Phase I TIE Study
Conclusions

- Effluent was more toxic at high pH than at neutral pH and reduction in pH was accompanied by a decrease in toxicity;
- Effluent pH and total ammonia concentration was in the toxic threshold range for trout;
- Reduction in daphnid toxicity with pH 11 filtration and EDTA tests suggested that residual daphnid toxicity at pH 7 was mostly due to metals, however, specific metals not identified.

1995 Phase I TIE Study
Conclusions

- Toxicity was reduced with lower pH and that the pH of the effluent and total ammonia concentration was in the toxic threshold range for trout;
- pH adjustment was the main factor in altering the effluent toxicity to rainbow trout;
- cationic metals were not a likely source of toxicity, but could not be ruled out as a possible secondary source of toxicity.

Objectives

1) To determine toxicity to rainbow trout and *Daphnia magna* after using sulfuric acid to adjust the pH of alkaline effluents from the Copper Cliff Waste Water Treatment Plant (CCWWTP) to levels < 9.5.

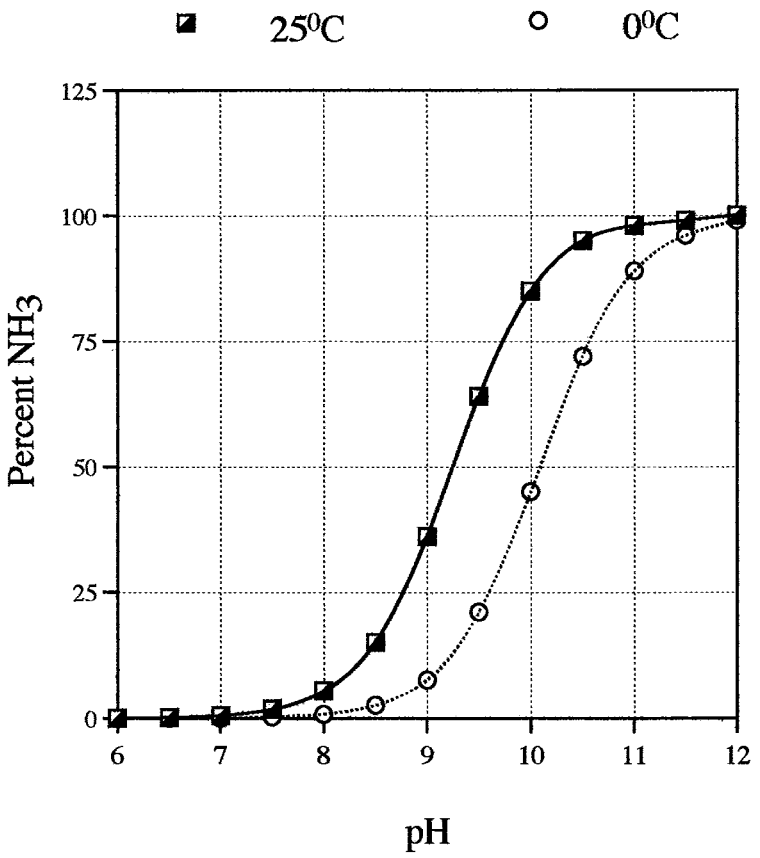
2) To confirm the primary role of carbon dioxide uptake in the reduction of alkaline effluent pH during bioassay tests.

Ammonia Toxicity and pH

$NH_3 + H_2O \longleftrightarrow NH_3 \bullet H_2O \longleftrightarrow NH_4^+ + OH^-$

$\longleftarrow$ increasing pH

$\longleftarrow$ increasing temp.



Percent of non-ionized ammonia (NH_3) present in aqueous solutions at temperatures of 25 and 0°C.

Cause of pH decline

Oxidation of thiosalts via *Thiobacillus* sp.?

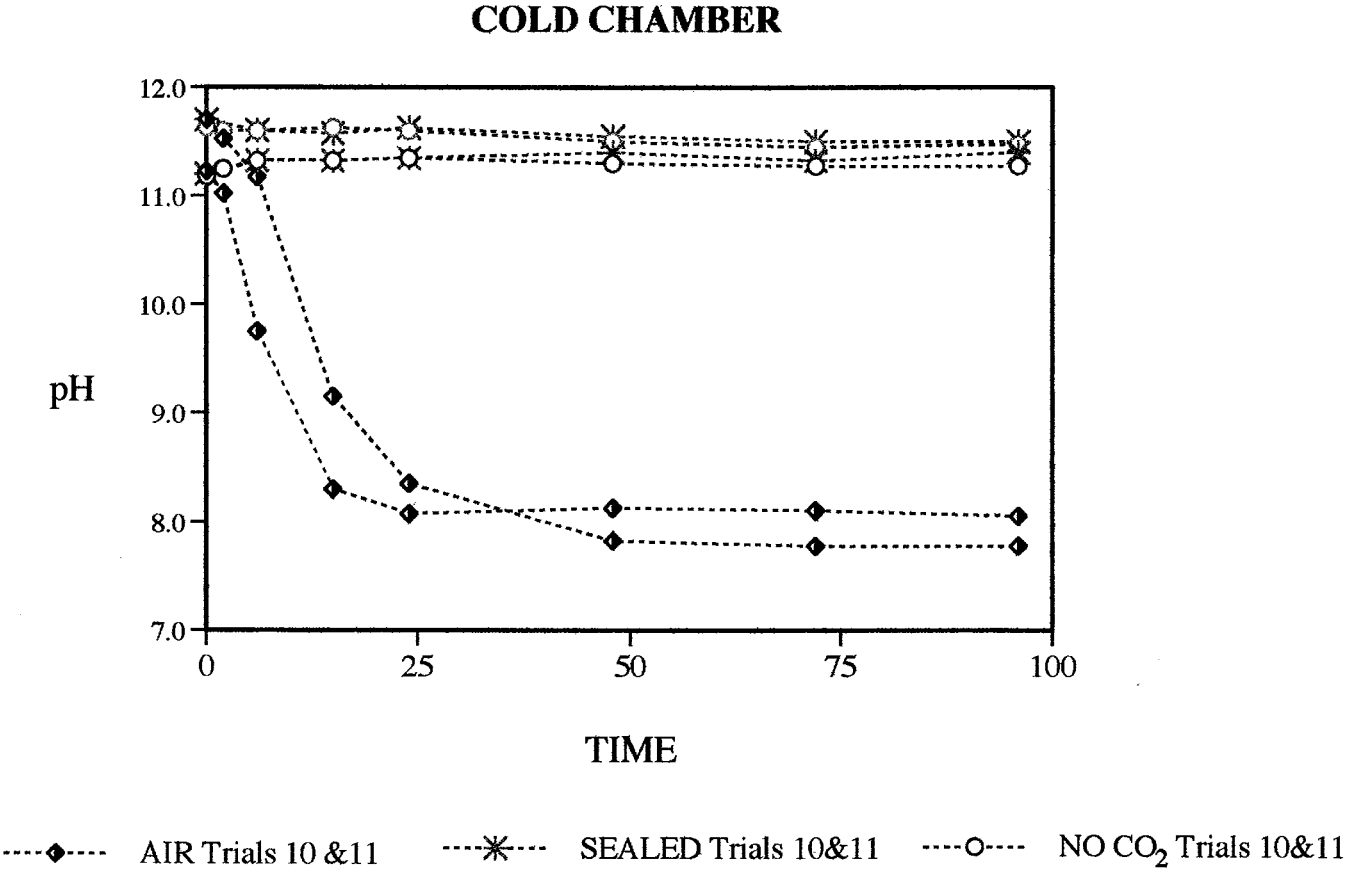
- **pH 2-8 and temperature range 20-43 ^{o}C required for optimal growth.**

CO_2 imbalance in effluent?

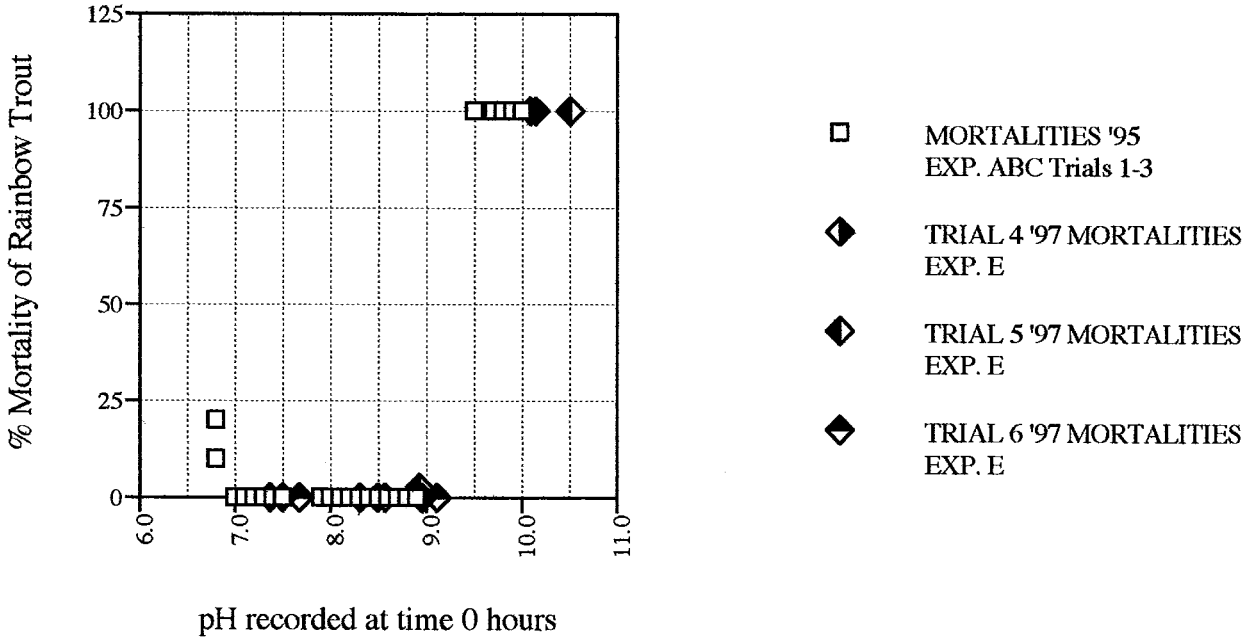
$$CO_2 \text{ (atmospheric)} + H_2O \text{ (effluent)} \longleftrightarrow H^+ + HCO_3^- \quad (1)$$

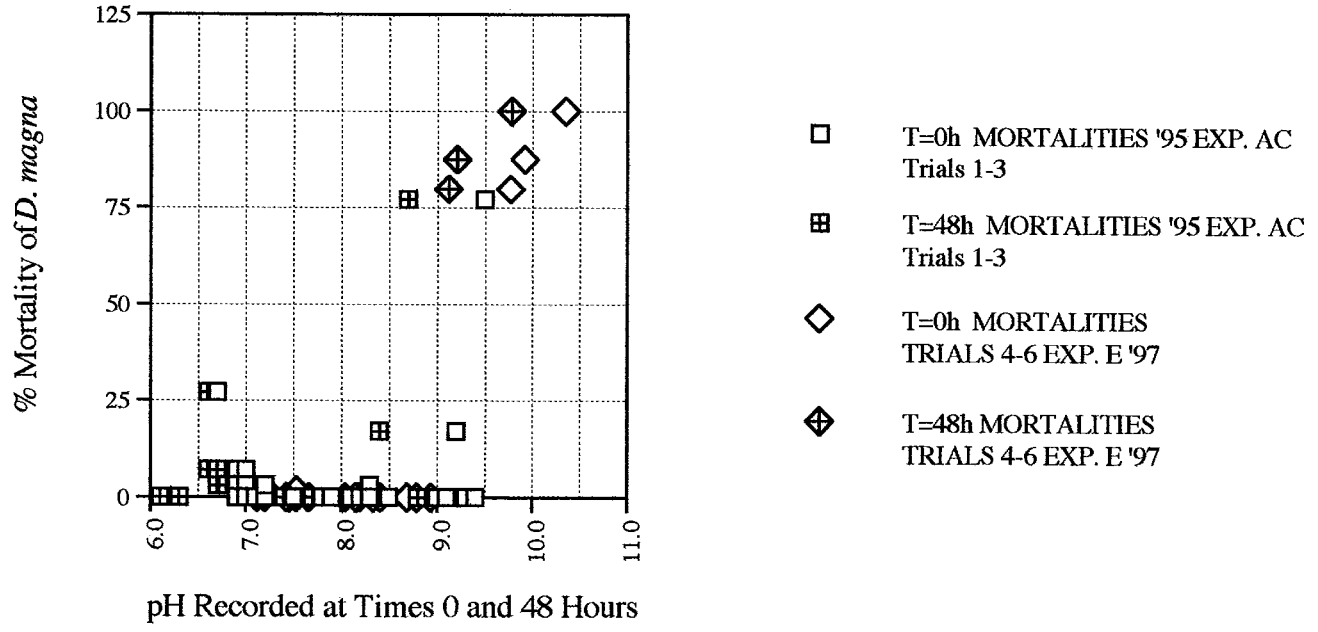
$$Ca^{++} + 2OH^- + 2H^+ + CO_3^{--} \longleftrightarrow Ca^{++} + CO_3^{--} + 2H_2O \quad (2)$$

- base thus begins to be neutralized.

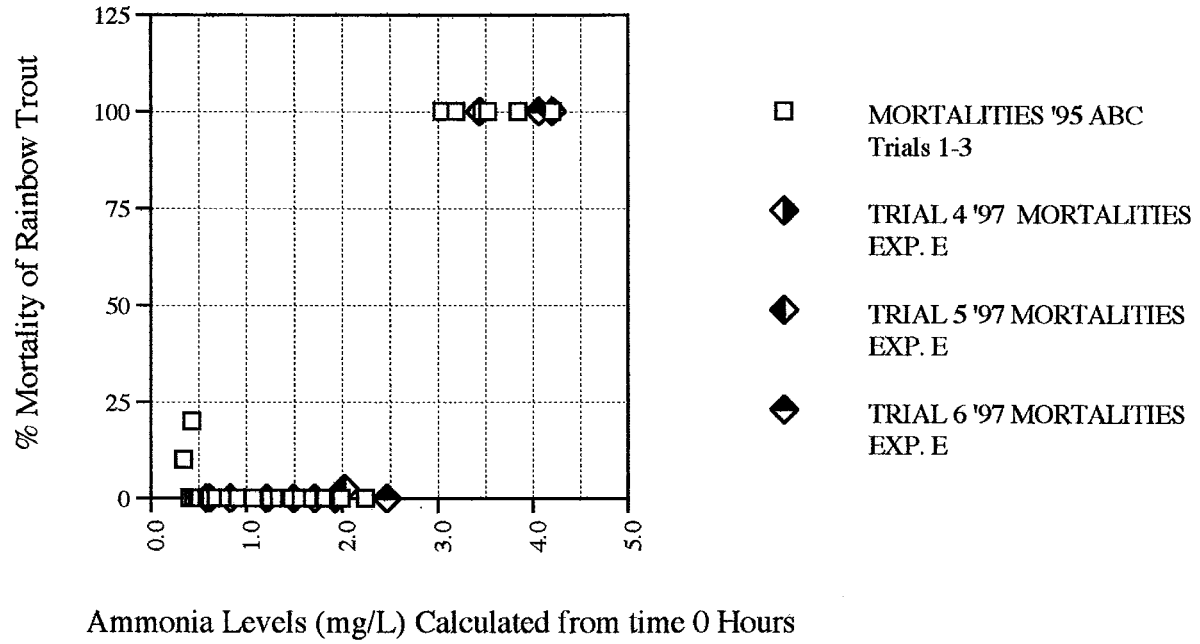


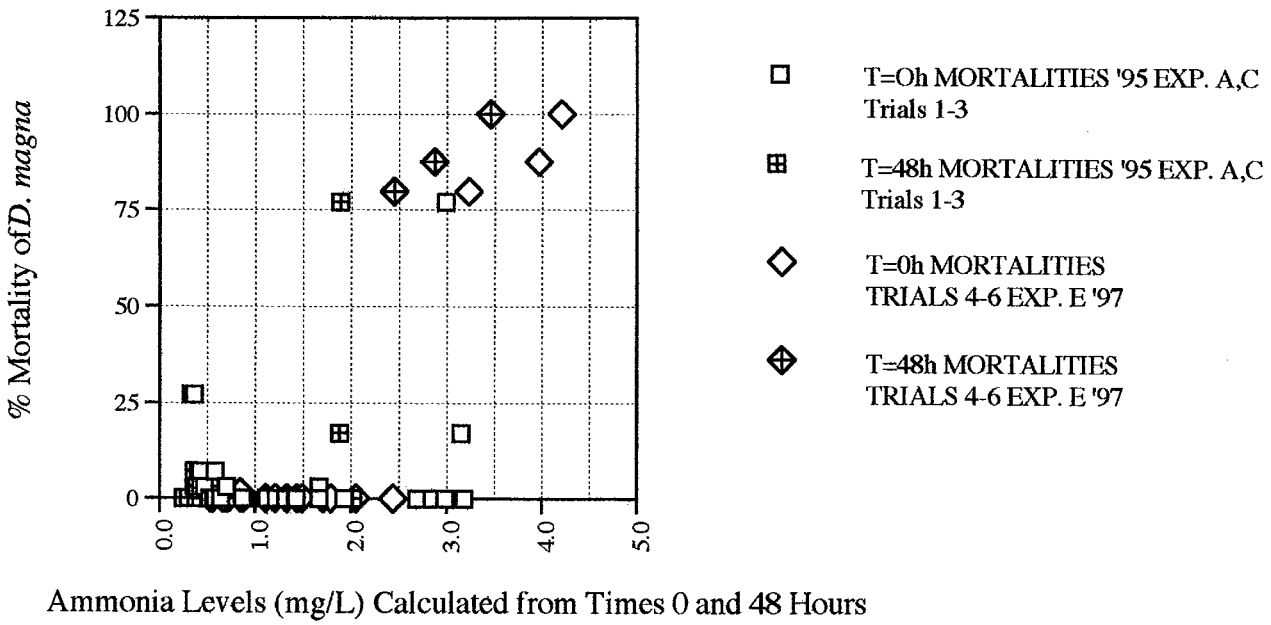
Observations of pH recorded over 96 h for trials 10 and 11 for manipulations of aeration, sealed, and CO_2 absent samples. Observations of pH for each trial time interval were based on means (n=4). Standard error for means were <0.16.





Scattergram of results of pH determined at critical periods of mortality for trout and *Daphnia* toxicity tests.





Scattergram of results of ammonia calculated at critical periods of mortality for trout and *Daphnia* toxicity tests.

pH Declines and Mortality: Considerations for assessing pH and ammonia related toxicity

- **Total ammonia, temperature, and pH variables required for the calculation of non-ionized ammonia (Emerson *et al.* 1975).**

- **Total ammonia values were utilized for each trial prior to toxicity testing.**

- **Temperature was constant for bioassay tests ($15^{o}C$ trout ; $20^{o}C$ *Daphnia*)**

pH ?

- **Mortalities were determined to be within 15 hours for trout. (observed within 2 hours in some instances)**

- **Mortalities were determined only upon completion of *Daphnia* tests (48 h). Indications of stress (immobility) were observed early into testing < 24h.**

- **Consequently, pH measured at t=0h for trout and t=0h and 48h for *Daphnia* was used to assess pH and ammonia toxicity.**

Assessment Problems

- **Lack of replication in previous studies**
- **Inconsistencies in toxicity results in identical effluent samples**
- **The recurrence of spontaneous decline of pH in effluent samples**

Observations

- Alkaline non pH adjusted effluents were highly toxic to both rainbow trout and *D. magna.*
  (Failure criterion for static acute tests **> 50%** mortality)

- Test failures were eliminated from every level of pH adjustment. (ie. **pH 9.3- 7.6**)
  (mortality rates were generally **≤ 10%**)

- Mortality rates observed in experimentally filtered effluents (0.45 μm) were not significantly different from non filtered effluents.

- pH declined after initial pH recorded and continued to descend during the course of toxicity testing.

Summary

- Toxicity in alkaline effluents was highly associated with high pH and elevated ammonia.

- Recommend that effluent be pH modified with H_2SO_4 to 8.7-8.9 to significantly reduce toxicity of effluent to both trout and *D. magna.*

- pH declines during toxicity testing were associated with carbon dioxide imbalance in effluent.

- Recommend that sample aeration protocols be uniform to ensure consistency in effluent toxicity testing.