Ammonia removal from recycled fish hatchery water

by Robert Dodd Braico

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Civil Engineering
Montana State University

Abstract:
The objective of this study was to evaluate the potential of clinoptilolite for removing ammonia from fish hatchery water. Since ammonia in concentrations at least as low as 0.3 mg/l NH_4^+ is toxic to salmonids, an effective means of removal is a prerequisite to reuse. A literature search indicated a specially constructed trickling filter is the only ammonia removal device now being used at fish hatcheries.

Ammonia removal by clinoptilolite was studied by passing synthetic wastewaters downward through a 12 in. deep by 1 in. diameter bed of zeolite at 20 bed volumes/hr.

The effect of brine concentration on regeneration was determined by passing various sodium chloride concentrations with 0.025N± of $Ca(OH)_2$ upward through the zeolite at 10 BV/hr.

Ammonia capacity of clinoptilolite is not linearly dependent on influent competing cation concentrations. A five fold decrease in run length accompanied a sodium concentration increase of 256 fold (0.067 me/l to 17.2 me/l).

Results of exhaustion studies at 12.5°C and 23°C were nearly the same. Similar results were obtained in regeneration studies. Therefore, room temperature investigations may be used to predict results in the temperature range of salmonid propagation.

The cost of ammonia removal for a 3500 gpm hatchery was estimated to be $0.031/1000 gallons with a water similar to Bozeman tap-water with 2.5 mg/l NH_3. A regenerant consisting of 0.10 N NaCl and 0.025 N $Ca(OH)_2$ was used for the cost estimate.

Extensive studies on the effect of competing ion concentrations are needed for accurate predictions with various waters. In addition the use of physical-chemical treatment for BOD removal should be studied in conjunction with ammonia removal by clinoptilolite.

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Signature Robert Dodd Burns

Date August 1, 1972

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Approved:

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Chairman, Examining Committee

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ABSTRACT

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CHAPTER I

INTRODUCTION

Artificial fish propagation is necessary to meet commercial and sport fishing needs where natural reproduction is either lacking or insufficient. Natural reproduction may be non-existent or poor for several reasons. Some of them are:

(1) Migration routes may be blocked by dams or pollution.

(2) Stream channelization may eradicate former spawning areas, suitable habitat, or both.

(3) Pollution may make spawning ineffective. Eggs and fry may be unable to survive because their requirements are generally more demanding than those of adults.

(4) Pollution may eradicate desirable species, making the stream or body of water valueless as a fishery. Therefore, demands upon remaining fisheries are increased, sometimes beyond their capacities.

(5) Commercial and sport fishing needs may exceed the supply by natural propagation.

These are some of the reasons justifying artificial fish propagation. Thus, just as surely as fishermen's demands increase, so will hatchery operations (Larmoyeux, 1968).

One of the problems associated with fish hatcheries is the apparent lack of suitable sites. Burrows and Combs (1968) over-zealously state natural sites which meet even two or three of the following major criteria for fish hatchery water supplies are not available:

(1) A sufficient quantity for operation must be assured.

(2) The water quality should match the requirements of the reared species.

(3) Water temperature should remain within the range needed for optimum growth rate.

(4) Disease incidence must be low or absent.

(5) Potential sites must be suitably located in relationship to release points. No hatchery program is successful if fish cannot be transported to release points with low mortality rates (Colorado, 1967). To meet these needs, recycling has been proposed by Burrows and Combs (1968).

A serious consideration with any recycle system is the accumulation of ammonia, a principle metabolic product of fish. Since it is well established that ammonia in only trace amounts can detrimentally effect salmonids, an economically attractive and reliable method is needed to provide almost total removal at the low levels in hatchery waters. All presently used ammonia removal methods appear to have one or more drawbacks in meeting these requirements. The writer proposes selective ion exchange is best suited for ammonia removal to low levels required in fish hatchery recycle water.

PURPOSE

The general aim of this study was to determine the potential of ion exchange for ammonia removal from fish hatchery recycle water. Clinoptilolite, a natural zeolite which is selective for ammonia, was compared with two non-ammonia selective resins with appreciably higher total capacity. More specifically, the purpose was to measure enough parameters for full scale design, including the effects of temperature, increased competing ions in solution, regenerant normality, and long term operation.

LIMITATIONS

Because exhaustion runs were long, it was necessary to design the study to meet the time constraint without seriously compromising results. Even with bed depths of 12 in., a single column run required from two to seven days. Only enough work was done with the two synthetic resins to establish the superiority of clinoptilolite.

Additional limitations of this study were:

(1) A feedwater concentration of 2.5 mg/l NH_3 was assumed to represent a typical hatchery effluent concentration and was used for all runs.

(2) All clinoptilolite exhaustion studies were run at 20 BV/hr (bed volumes/hr).

(3) Two feedwaters were used to measure the effect of sodium concentration on clinoptilolite ammonia capacity.

(4) All regeneration studies were restricted to clinoptilolite.

(5) Only regenerants containing NaCl and $Ca(OH)_2$ were considered.

(6) One exhaustion and one regeneration run were made within the low temperature range applicable to salmonid hatcheries.

SYMBOLS

Symbols are defined when first used. They are defined again in Appendix A.

CHAPTER II

AQUEOUS AMMONIA

Ammonia, rather than ammonium ion, is responsible for the debilitating effects on fish. The significance of pH and temperature on the NH_3 - NH_4^+ ratio is shown in Figure 1. The equilibrium of aqueous ammonia is given in Equation 1.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-, \ K = 1.8 \times 10^{-5} \quad (1)$$

Wilbur (1969) reported a pH shift from 7.4 to 8.0 resulted in at least a 200% toxicity increase.

EFFECT ON SALMONIDS

Fromm (1970) stated the toxicological effects of ammonia on fish are not completely known. However, he felt toxicity was due to the prevention of normal ammonia excretion and that the nervous system was earliest affected. In a study of rainbow trout exposed to various ammonia concentrations, a direct linear relationship between total blood ammonia concentration varied from 0 to about 9 mg/l and the corresponding range of total blood ammonia varied from 25 to 85 mg/ml.

Studies by Brockway (1950) showed an increase in ammonia concentration resulted in reduced blood oxygen and based on this, he suggested ammonia reduces the ability of blood to transport oxygen.

Studies at the Fish Cultural Development Center, Bozeman,

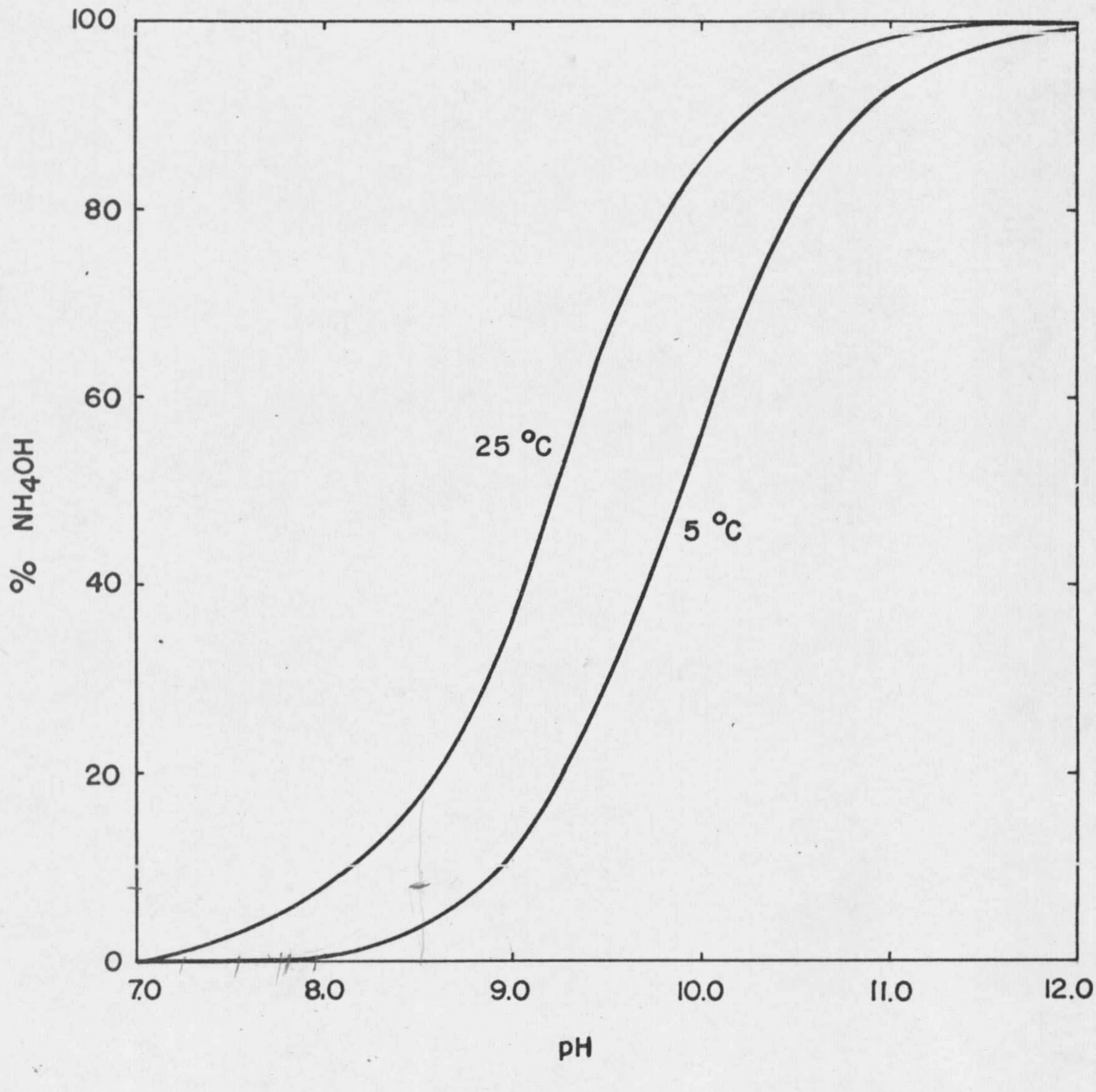

FIGURE I. PERCENT NH_4OH IN WATER AS A FUNCTION OF pH