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Removal of sodium thiosulfate from wash water by the use of ion exchange resins for application in a closed photographic system

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REMOVAL OF SODIUM THIOSULFATE FROM WASH WATER
BY THE USE OF ION EXCHANGE RESINS
FOR APPLICATION IN A CLOSED PHOTOGRAPHIC SYSTEM

by

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If anything can go wrong with an experiment ...

it will

ABSTRACT

Ion exchange resins were used for removing sodium thiosulfate from wash water. Quantitative tests were run to determine the feasability of using the resins in a closed rapid processing system. One liter of a monobed resin and one liter of an anion resin, each in a separate ion exchange column, were found to be sufficient to remove the sodium thiosulfate left in the wash water for 8000 square inches of Kodabromide F-2 paper under specified conditions.

BACKGROUND

It would be desirable for the amateur photographer to have facilities for immediate obtainability of finished photographic prints without the necessity of special camera equipment. This could be accomplished with a self-contained, continuous rapid processing machine. Designing such a machine would involve both mechanical and chemical problems. The chemical problems would include the processing of the photographic material and its effective washing. Suitable rapid processing solutions are commercially available which could be adapted to such a system. The major chemical problem in such a system would be the washing of the material.

OBJECTIVE

The objective of this work is to devise a method of washing photographic materials in a closed system in which a quantity of wash water would be reused.

EXPERIMENTAL PROCEDURE

Analysis of Hypo Content in Wash Water

A given quantity of photographic paper, 1000 square inches, was exposed and processed in Kodak SD-10 developer for 70 seconds, rinsed in 28% acetic acid and placed in F-7 fixer for 1 minute. The temperature was maintained at 24°C.

The prints were washed in 2 liters of water at 24°C with constant agitation for 5 minutes. They were then squeegeed and placed in another tray containing 2 liters of water. The same procedure was followed until the prints had been washed in 8 trays of water (16 liters). After each 5 minute wash a 1"x 2" sample was taken from a large border area of a randomly selected print and identified.

A quantitative test for residual thiosulfate ion was run on the samples, as described by Crabtree, Eaton and Muehler.[1]

The 2 liter quantities of wash water were combined and quantitatively analyzed for sodium thiosulfate content.[3,4]

A test was run to determine the allowable sodium thiosulfate concentration in wash water for commercially acceptable prints. Solutions of varying low concentration of sodium thiosulfate were mixed and completely washed samples of photographic paper were placed in each for 30 minutes.

The test for residual thiosulfate content was run.[1,2]

Ion Exchange System

A 0.1 N solution of sodium thiosulfate was passed through an ion exchange column containing a monobed made up of 500 ml of Amberlite IRA 410 anion exchanger and an equal volume of Amberlite IR 120 cation exchanger. The effluent from this column was then passed through a column containing 1 liter of Amberlite IRA 400 anion exchanger. The direction of flow was from top to bottom in the monobed and from bottom to top in the anion bed. A flow rate of 200 ml/minute was maintained. 100 ml of the effluent from the system was taken at 500 ml intervals. These 100 ml samples were each analyzed for sodium thiosulfate concentration.[3]

EXPERIMENTAL RESULTS

Sodium Thiosulfate Content of Processed Kodabromide F-2 (1000 square inches)

Time of Washing	Total amount of Wash Water Used	$Na_2S_2O_3$ Residual mg/in^2
5 minutes	2 liters	0.30
10 "	4 "	0.17
15 "	6 "	0.10
20 "	8 "	0.10
25 "	10 "	0.10
30 "	12 "	0.09
35 "	14 "	0.10
40 "	16 "	0.10

Normality of the 16 liters of wash water was 0.005 N.
Sodium thiosulfate content of the 16 liters was 20 grams.

Capacity of Ion Exchange System Containing 1 liter of Monobed Resin and 1 liter of Anion Resin.

The volume of 0.1 N sodium thiosulfate influent is plotted against the normality of the effluent in Figure 1.

Tests for Allowable Sodium Thiosulfate Concentration in Wash Water That is to be Used for Commercial Quality Washing of Prints.

Normality of $Na_2S_2O_3$ (Wash Water)	$Na_2S_2O_3$ concentration in Prints - mg/in^2
.005	.05
.007	.07
.010	.10
.014	.14

Commercial quality prints should contain a maximum of 0.15 mg/in^2 of residual sodium thiosulfate.[1] Then, wash water with a sodium thiosulfate concentration of 0.01 N can be used to effectively wash prints. This places the cut-off point on the graph (Figure 1) at 6.5 liters of 0.1 N sodium thiosulfate. From this the capacity of the system is calculated to be 160 grams of sodium thiosulfate. Since the wash water from washing 1000 square inches of Kodabromide F-2 paper contained 20 grams of sodium thiosulfate, the amount of paper that can be washed to commercial quality with the specific quantities of resins used would be 8000 square inches.

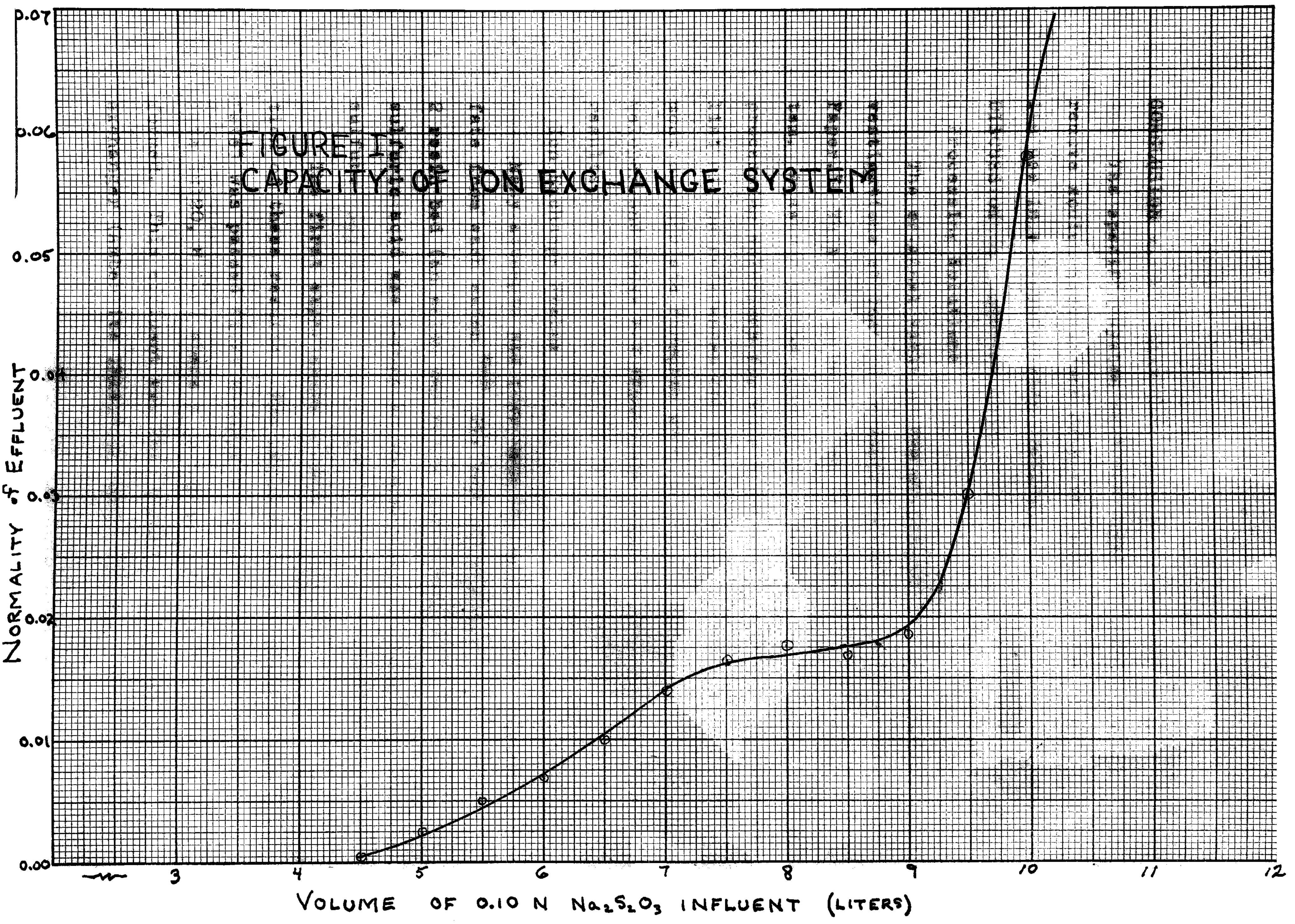


FIGURE I
CAPACITY OF ION EXCHANGE SYSTEM

CONCLUSION

The specific system used was found to sufficiently remove sodium thiosulfate from wash water so as to make its use in a closed system feasible.

DISCUSSION

Processing Solutions

The original title of the project was "Chemical Investigations of Continuous Rapid Processing of Film and Paper." This was to be applied to a specific closed system. A search of the literature provided satisfactory processing solutions for such a system.[5-7] For a complete list of the references see the project notebook.[2] The most appropriate formulas were tested and Kodak SD-10 developer and Kodak F-7 fixer were found to give acceptable results.

Ion Exchange Resins

Many attempts had been made to remove sodium thiosulfate from wash water.[8-9] The problem encountered using a 2 resin bed (an anion bed and a cation bed) was that thiosulfuric acid was formed which decomposed to form colloidal sulfur.

The first experiments in this project were a duplication of these results. The influent (0.1N sodium thiosulfate) was passed first through a cation exchanger (Amberlite IR120, H ion) where a yellow sulfur precipitate was formed. This effluent was then passed through an anion exchanger (Amberlite IRA410,OH ion). This effluent was cloudy and white. When the procedure was rerun with the anion bed being used first the effluent from the anion bed was found to be clear and of very high pH due to the sodium hydroxide formed. Also the anion bed did not remove all the thiosulfate ion since sulfur was formed in the cation bed.

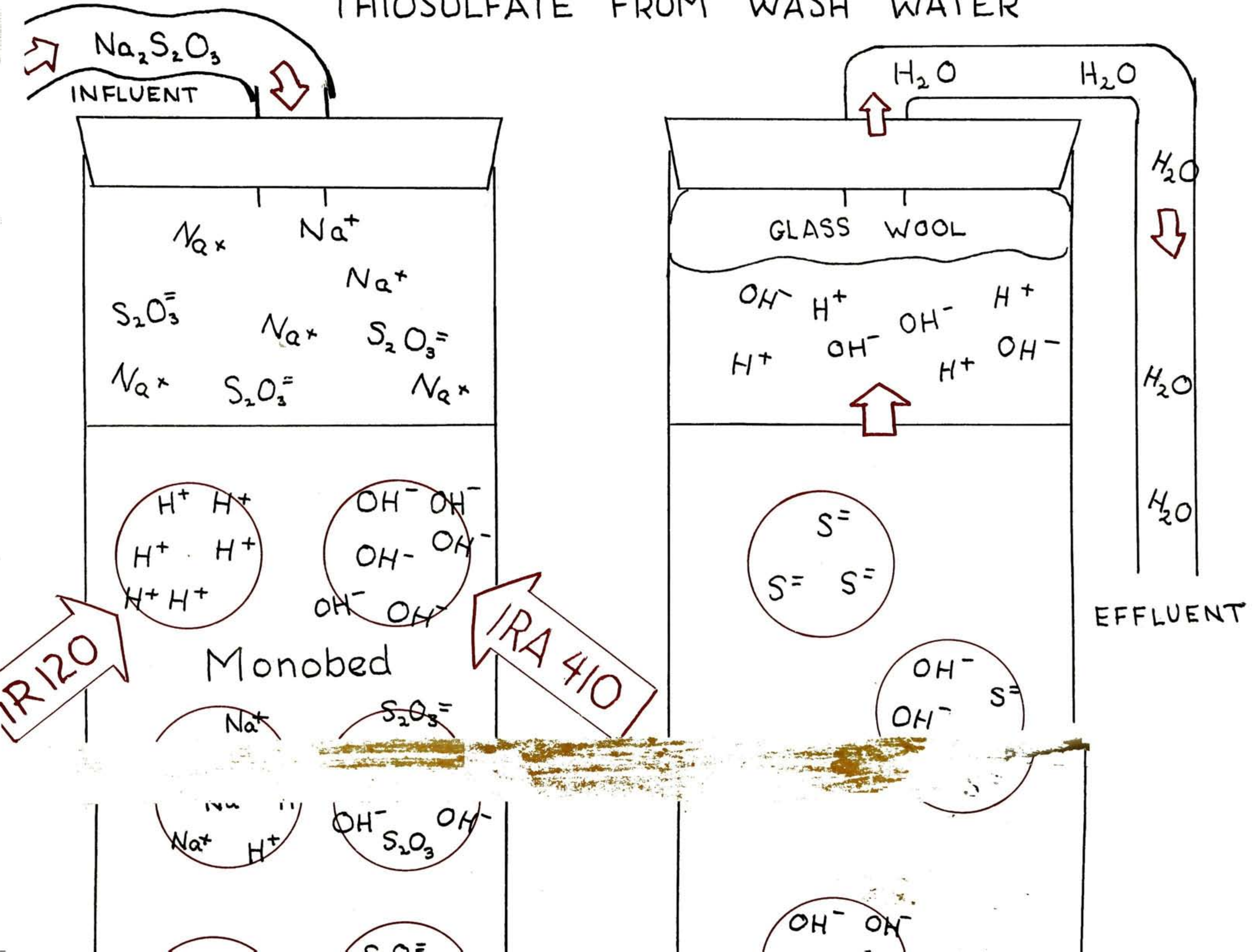
A monobed was mixed containing equal amounts of anion (IRA410) and cation (IR120) exchange resins. The same influent was passed through this bed. The effluent although clear contained hydrosulfuric acid. When this was passed through another bed containing only an anion bed (IRA400, OH ion), the sulfur was removed and the effluent was neutral.

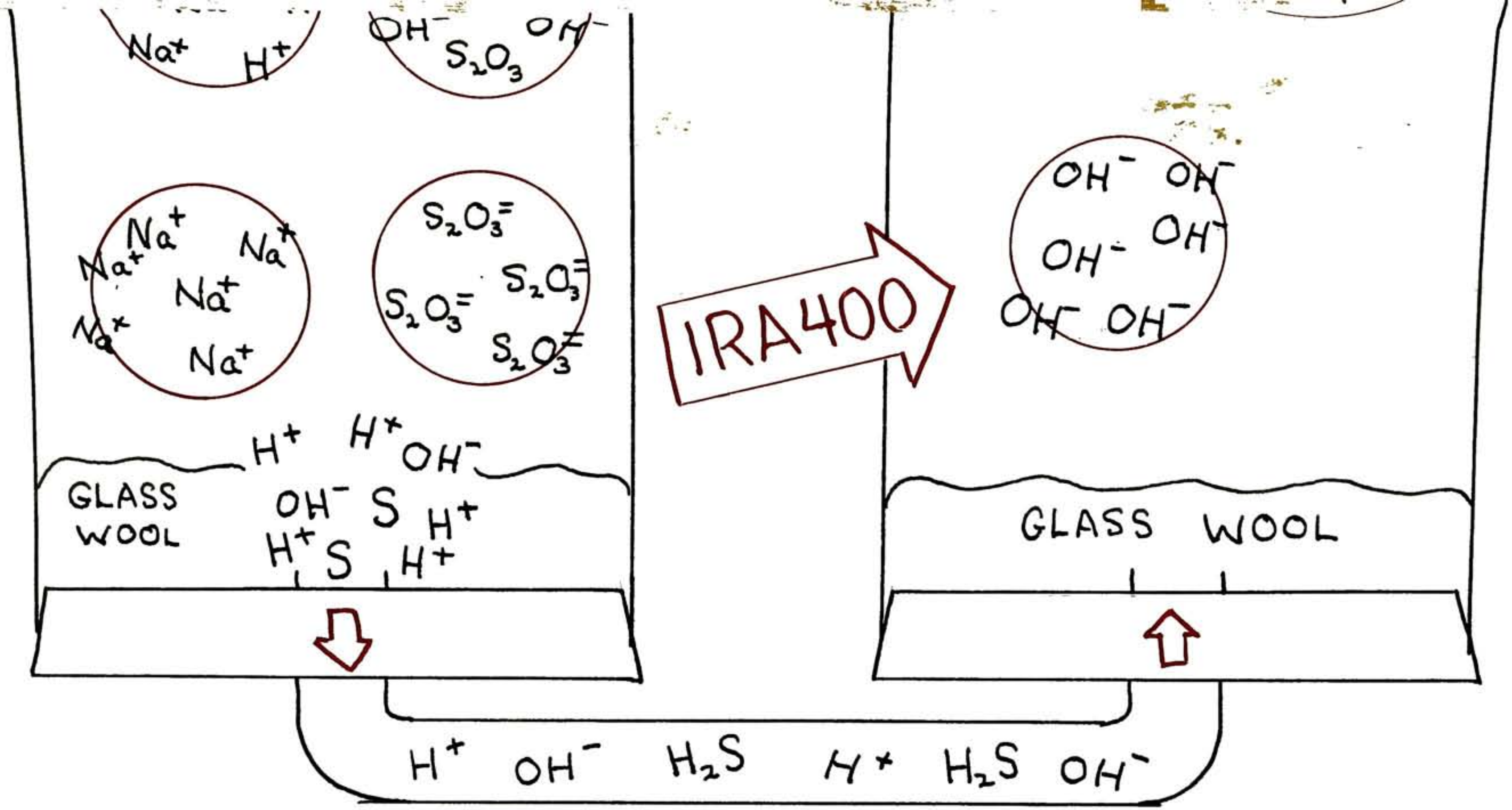
The desired direction of flow in an ion exchange column is from bottom to top.[10] This prevents the resins from packing in the column and keeps them in motion with the surface exposed to continually moving solution. However, in a monobed this is not possible because circulation separates the anion and cation resins. This is very useful for rejuvenating the resins but when using the monobed, it is necessary to pass the solution from top to bottom in the column.

A sodium thiosulfate solution of much greater concentration than that found in wash water was used to determine the capacity of the ion exchange resins. Since the capacity of the resins for sodium thiosulfate is relatively large, a very dilute solution such as is found in wash water would require a prohibitively long titration analysis. Since the reaction is quantitative the concentrated solution may be used to determine the capacity of the resins for a more dilute solution.

In determining the capacity of the ion exchange resins sodium thiosulfate solution of known normality was used instead of used hypo-water solution. Even though the latter would conform more to practice, it was felt that a more quantitative result could be obtained if the bed was analyzed for sodium thiosulfate alone. Naturally it would be desirous to know how the bed is effected by the other constituents of hypo plus silver complexes but the limited scope of the project did not include such a test.

FIGURE II. ION EXCHANGE RESINS REMOVING SODIUM THIOSULFATE FROM WASH WATER





$$Na_2S_2O_3 + H_2O \rightarrow Na^+ + S_2O_3^=$$

$$IR\,120(H^+) + Na^+ \rightarrow IR\,120(Na^+) + H^+$$

$$IRA\,410(OH^-) + S_2O_3^= \rightarrow IRA\,410\,(S_2O_3^=) + OH^- + S$$

$$H^+ + OH^- + S \rightarrow H_2O + H_2S$$

$$IRA\,400(OH^-) + H_2S \rightarrow IRA\,400(S^=) + H_2O$$

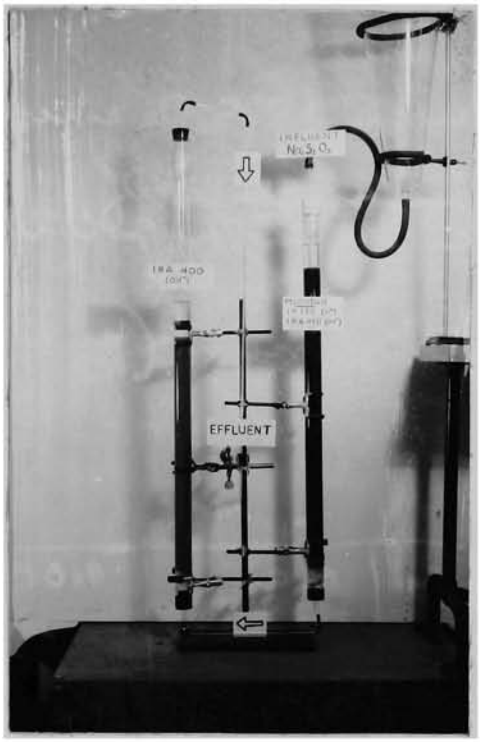


FIGURE III.

ION EXCHANGE SYSTEM

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