DETERMINATION OF PORTION OF THE RECOVERY BRINE TO BE USED AS THE PRELIMINARY TREATMENT IN REGENERATION OF THE ZEOLITE SOFTENERS EAST LANSING

Thesis for the Degree of B. S.

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Water-Softening

Determination of Portion of The Recovery Brine To be Used as The Preliminary Treatment in Regeneration of The Zeolite Softeners

(East Lansing)

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L.H.R.

INTRODUCTION

Zeolites have been used for over 25 years in this country and abroad for water softening. During this period, the application of this method of water softening has grown to be an industry of world wide scope. In addition to their use for softening industrial waters for laundry , textile, boiler feed, etc., zeolites have established a definite place in the field of water softening for general use, such as is required in the home. This has been reflected in the steady increase in the number of installations made for this purpose, until they now total well over 150,000. More recently, the tendency to use zeolites for general purposes has made itself evident in the increasing number of installations made by municipalities in order to give entire communities the benefits of zeolite softened water.

One of the most important characteristics of zeolite softened water is the fact that there is no sludge formed during softening as there is in other methods of softening water. The advantage of having no sludge formed is that it enables the plant to be located in a limited area where-as if sludge is to be disposed of it would require a much larger area.

The economy of operation of a zeolite plant depends mainly upon the cost of salt, therefore in order to operate most economically an effort must be made to economize as much as possible in its use.

In a zeolite softener, after the tank has become exhausted of its softening capacity, the zeolite must be regenerated. This regeneration is accomplished by passing salt brine through the zeolite sand bed which restores the zeolite to its original form (NaZ).

At the East Lansing, Michigan water softening plant, a definite volume of a saturated salution of salt brine is pumped into the zeolite softening tank then it is rinsed out. The rinse water is pumped into a brine recovery tank and is used as a preliminary treatment in the regeneration of the succeeding tank. At the present time the rinse period is about 22 minutes of which the first 16 minutes of flow is saved the remaining portion being allowed to discharge into the sewer.

As far as this investigation could determine there has been no work done to determine whether or not there is any advantage in the using of the rinse water, from a newly brined tank, as a preliminary treatment in the brining of a succeeding tank, and if there is any value in the rinse just what portion of it should be saved.

In this paper an attempt has been made to determine if there is any value in the recovery brine as well as determining which portion of the rinse it is best to save in order to secure the best part of the rinse.

DESCRIPTION OF E. LANSING WATER WORKS

EAST LANSING MICHIGAN

The water works is located on the west side of town and serves a population of approximately 8000. The water is obtained from 2 deep wells, which are 420 feet deep and 12 inches in diameter. The casing is sunk to a depth of 180 feet with a strainer at a depth of 169 feet from the floor of the pumping pit, which is about 10 feet below the surface of the ground.

The waters obtained from these two wells are of excellent sanitary quality. Chemically they are hard waters and also contain objectionable amounts of iron and free carbon dioxide both of which are corrected at the plant and will be discussed later.

The hardness is the most objectionable characteristic of the water. It is softened by passing it through beds of sodium zeolite, which process will be discussed later. Hardness results in a very large waste of soaps as the hardness must be overcome by the soap before any lather is formed. Hard water also causes incrustations to be formed on the inside of hot water pipes, which results in inefficient heating and reduced capacity.

Before entering into the discussion of the operation of the plant we should first determine just what constitutes soft water.

Soft water is a relative term and it was first brought to the public eye by the variation in the amount of soap required to produce a lather in water. The consumer judges the water to be hard if much soap is required to produce a lather, and soft if it lathers freely. Investigations have shown that hardness in water is directly proportional to the amounts of the following minerals in the water.

(a) Calcium bicarbonate (limestone).

(b) Magnesium bicarbonate (magnesite).

(c) Calcium sulfate (gypsum).

(d) Magnesium sulfate (epsom salts).

Accordingly, a water having a large amount of these minerals is termed a hard water, while one with a low content is termed "soft". It is generally conceded throughout water works literature, that a water containing less than 100 parts per million of the above mentioned minerals expressed as calcium carbonate ($CaCO_3$) is soft, while anything over that amount is considered hard. It is therefore necessary to remove these minerals in order to obtain a soft water, if they occure in sufficient quantity to pro-

duce hardness.

The iron content in the water is removed by passing it through beds of manganese zeolite. Iron in water results in discoloration of the water and stains plumbing fixtures. The iron content is reduced from 1 part per million to less than 0.1 part per million. The zeolite consists of sodium zeolite that has been treated with manganese chloride to convert it to manganese zeolite by base exchange, and then oxidized by sodium or potassium permanganate.

Reactions:-

$$Na_2OZ + MnCl_2 = MnOZ + 2NaCl$$

$$MnOZ + 2NaMnO_4 = Na_2OZ + MnOMn_2O_7$$

The higher oxides of manganese formed in the second reaction are carried to the surface of the grains of the zeolite. When water containing iron is passed through the sand, these oxides give up oxygen to the water.

Reactions:-

$$MnOZ + MnOMn_2O_7 + 4Fe(HCO_3)_2 =$$
$$MnOZ + 3MnO + 2Fe_2O_3 + 8CO_2 + 4H_2O$$

There are two storage reservors in the distribution system. The one on the east side has a capacity of 100,000 gallons and the one on the west side with a capacity of 50,000 gallons. This amount is much too small for a city the

size of East Lansing due to the fact that a certain amount of water must be left in the bottom of the tank to act as cushion, which leaves an available storage capacity of about 100,000 gallons, which will supply only two hours flow at average demand.

Pumpage varies from 350,000 gallons per day in the winter to from 800,000 to 1,000,000 gallons per day in the summer. The pressure at which the water leaves the station is approximately 50 pounds per square inch. Water leaves the plant through an 8 inch main and is distributed to the city through 8 inch, 6 inch, 4 inch, and 2 inch pipes.

The water treatment plant forms a part of the distribution system. The water comes directly from the wells to the plant where three-fourths of it is passed through the softening units and the remaining portion is passed through the iron removal units.

The two water pumps are of the centrifugal type, one being a five stage and the other is a six stage.

As was previously stated in this paper the main treatment of the water is that of softening, which is accomplished by means of zeolite softeners.

The plant consists of a battery of 5 zeolite softening tanks each of which contains 200 cubic feet of zeolite sand. The zeolite sand costs $5.00 a cubic foot. The tanks are 7 feet in diameter and are 9.0 feet high, "straight sides". Three fourths of the water is passed through these 5 tanks and is softened to zero hardness.

$\frac{\pi \times 49}{4} + 9 = 346$ cu ft

There are also two tanks of the same size, each of which contains 100 cubic feet of zeolite sand, and it is the sole purpose of these tanks to remove the iron from the remaining portion of water that is not passed through the 5 softening tanks.

The first step in the operation of the plant is that of softening the water. Raw water (untreated well water) enters the top of the tank through a 3 inch pipe. The water passes downward through the zeolite sand bed during which time the water is softened to zero hardness by means of the hardness compounds being replaced by the non-hardness compounds, and the iron content is also reduced at the same time.

The softened water enters a set of small orifices at the bottom of the sand bed and then enters a 3 inch pipe through which it leaves the softening tank and joins the flow from the other softening units.

After a definite time interval, equivalent to the passage of 28,000 gallons of water through the tank, the zeolite sand in the tank has practically exhausted its softening capacity and is ready for regeneration, the first step of which is washing the sand.

By means of an automatically electricly operated multiport valve, the raw water is now directed into the tank through a 3 inch pipe and orifice system in the bottom of the tank. Water passes upward at a sufficient velocity to wash out material deposited during the softening operation. The wash water leaves the tank through a 3 inch pipe at the top of the tank and flows into the sewer. The rate of wash is controlled by an orifice-constant-head-box, with a float controlled valve. After a definite time interval of washing (10 minutes at 230 gallons per minute for this plant) the tank is ready for its next step in operation, which is dosing with brine.

The automatic multiport valve now opens and closes the proper valves for dosing with brine, and the brine pump automatically starts to pump brine from the brine recovery tank. This brine is the used brine from the rinsing of the previously regenerated tank. This recovery brine enters the tank through a pipe near the top of the tank, and flows down through the zeolite sand and the effluent from the tank is discharged into the sewer. This old brine is pumped at a rate of 115 gallons per minute for a period of 15 minutes. When the brine recovery tank has been emptied a float switch shuts off the brine pump and opens a diaphram valve on a water pressure line just ahead of an ejector, which operates to pump new brine from the brine measuring tank.

Brine from the brine measuring tank is pumped by the ejector to the top of the softener and flows down through the zeolite sand, the effluent from the tank going into the sewer. This flow continues until the proper amount of saturated brine is added to the tank (7903gallons), after which a float switch closes the diaphram valve on the water pressure line near the ejector, opens the diaphram valve on the brine pipe from the brine storage, closes the diaphram valve on the brine inlet pipe near the top of the softener tank and actuates the multiport softening tank valve to the rinse position.

In the rinsing operation, raw well water

goes in at the top of the tank through the 3 inch pipe. The used brine leaves through the 3 inch pipe at the bottom of the tank, enters an elevated rate-of-flow control box, which assures a uniform rate of flow during rinsing, from which it flows into the brine recovery tank.

After rinsing for a definite time interval (20 minutes at 115 gallons per minute) the multiport valve moves again to the softening position and a complete cycle of operation has been completed.

The fundamental principle in the operation of a zeolite softener is the base exchange process and is based on the following reactions:-

Softening:-

$$NaZ + Ca \text{ or } Mg(\text{salts}) = Na \text{ salts} + CaZ \text{ or } MgZ.$$

Regeneration:-

$$CaZ \text{ or } MgZ + NaCl = NaZ + CaCl_2 \text{ or } MgCl_2.$$

PROCEDURE OF CHEMICAL ANALYSIS OF SAMPLES

Chloride determination (volumetric method).

In this determination the chloride of the sample is determined by titration with a standard solution of silver nitrate in the presence of potassium chromate indicator. The chloride is precipitated as silver chloride (a white precipitate).

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

The end-point of the titration is reached when a brown precipitate of silver chromate first appears, due to the reaction of a slight excess of silver nitrate with the potassium chromate ($K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3$) a correction of 0.2 ml. is made for the excess silver nitrate required to produce a noticable amount of brown precipitate. Hydrogen sulfide interfers with the reaction precipitating black silver nitrate.

$$H_2s + 2\ AgNO_3 = Ag_2S + 2HNO_3$$

Procedure:-

1. Pipette 50 ml. of the sample into a porcelain evaporating dish.
2. Place about the same quantity of distilled water into a second dish for a color comparison.

3. Add 1 ml. of potassium chromate indicator to each.
4. Add standard silver nitrate solution to the sample from a burette, a few drops at a time, with constant stirring until the first permanent reddish coloration appears. This can be determined by a comparison with the distilled water blank.
5. If more than 7 or 8 ml. of silver nitrate solution are required, the entire procedure should be repeated using a smaller sample diluted to 50 ml. with distilled water. Record the ml. of silver nitrate used.

Calculations:-

$$\frac{(\text{ml. of } AgNO_3 \text{ used} - 0.2)500}{\text{ml. of sample}} = \text{p.p.m. Cl.}$$

Preparation of sample for determination of Calcium & Magnesium;-

Measure accurately 250 ml. samples of the water to be tested, add a few ml. of concentrated hydrochloric acid and evaporate to dryness in dishes over a water bath. Cool and moisten each residue with a few drops of concentrated hydrochloric acid. Add about 30 ml. of distilled water and heat to boiling. Filter through seperate filter papers, washing the dishes and the residues on the paper with small portions of distilled water, and add the washings to the filtrates. The volumes of the filtrates should be kept below 50 ml.

Removal of Iron & Aluminum Oxides:-

To the filtrate obtained from above add a few ml. of bromine water and boil for a few minutes. Add 20 ml. of 10 per-cent ammonium chloride solution and an excess of ammonium hydroxide. Boil for 5 minutes. Filter the solution through filter paper, rinsing and washing the beaker and filter paper with small portions of distilled water. Save the combined filtrate and washings for the calcium and magnesium determination, and discard the precipitate.

Calcium determination:-

Warm the filtrate obtained from the iron and aluminum determination, add 10 ml. of a saturated solution of ammonium oxalate drop by drop with constant stirring, (add more of the oxalate if it is required to precipitate all of the calcium), and set in a warm place for about 30 minutes. Filter and wash the beaker and the paper with hot distilled water. Save the filtrate and the washings for the magnesium determination. Pierce the filter paper and wash the precipitate into the original beaker with about 30 ml. of 2 per-cent sulfuric acid, (use a larger quantity of the acid if necessary to disolve all of the precipitate). (I also placed the filter paper in the beaker to make sure that all of the precipitate was obtained). Heat to boiling and titrate with standard permanganate.

Calculations:-

Ml. of $KMnO_4$ x 10 = p.p.m. calcium (Ca).

Magnesium determination:-

To the filtrate saved from the calcium determination, add concentrated ammonium hydeoxide in sufficient quantity to make about one ninth its volume. (Make definitly alkaline). Add 10 ml. of sodium acid phosphate solution, stir vigorously for five minutes, and allow to stand for at least four hours. Ignite, cool and weigh a crucible. Filter the precipitate onto a quantitative filter paper, wash with a weak solution of ammonia and place in the crucible. Heat in the oven at about 105 degrees until the filter paper and precipitate is thoroughly dry, then place in oven and ignite, cool and weigh.

Calculations:-

Gain in weight (grams) x 873.6 = p.p.m.(Mg) magnesium.

Determination of specific gravity:-

1. Dry and weigh an empty beaker of about 250 ml. capacity and weigh to the nearest 0.1 gram.
2. Pipette 100 ml. of the sample into the beaker and reweigh to the nearest 0.1 of a gram.

Calculations:-

$$\text{Sp. Gr.} = \frac{\text{Weight of sample}}{\text{Ml. of sample}}$$

Determination of sodium:-

1. Find the reacting values (R) of all the elements.

$$R = \frac{(\text{p.p.m. of the element}) \times 1}{\text{equivalent weight of element}}$$

2. Find the sum of the reacting values of both the negative and positive elements.
3. (Sum of negative R values - sum of the positive R values) x 23 = p.p.m. of sodium and potassium expressed in terms of sodium.

PREPARATION OF REAGENTS AND STANDARD SOLUTIONS

Aluminum hydroxide:-

Dissolve 125 grams of pure aluminum sulfate in one liter of water. Add ammonium hydroxide until the precipitation is complete. Allow to settle and pour off the supernatent. Wash the precipitate in a large quantity of d distilled water to remove chlorides, nitrates and ammonia.

Bromine water:-

Fill a liter bottle almost full of distilled water. In the hood, carefully pour about 10 ml. of bromine into the bottle. Stopper and shake. Care should be used in handling bromine as the liquid or its fumes cause serious burns.

Ammonium chloride:-(10 %)

Dissolve 100 grams of C.P. ammonium chloride in distilled and make up to one liter.

Saturated ammonium oxalate:-

Place about 50 grams of C.P. ammonium oxalate in a liter bottle and fill with distilled water. Shake and let stand until almost all of the crystals are dissolved. (Use the supernatent liquid.)

Sulfuric acid:-(2%)

Add 20 ml. of concentrated sulfuric acid to a liter of distilled water.

Standard potassium permanganate:-(0.125N)

Weigh out 3.95125 grams of stock standard potassium permanganate and dissolve in one liter of distilled water.

Disodium phosphate:- (10%)

Dissolve 100 grams of C.P. disodium sulfate (Na_2HPO_4) in distilled water and make up to one liter.

Iron Removal Tanks.

Three of The Five Softening Tanks.

DISCUSSION

As was stated before in this paper, the economy of operation of the softening plant (zeolite softeners), depends upon the price of salt and the amount used, and therefore, in order to operate most economically, economies must be affected as much as possible in its use. To do this, the brine used in the regeneration of a tank is being saved and used as a preliminary treatment of a succeeding tank.

It is the purpose of this thesis to determine just what portion of the rinse should be saved in order to secure the best part of the used brine.

In collecting the samples for this thesis, samples were taken at two minute intervals after the beginning of the rinse period of tank #3. The rinsing period lasted for about 22 minutes. Only the first 16 minutes of the flow during the rinse period is saved at the present time, the remaining portion being allowed to discharge into the sewer.

Tests were run on these samples to determine the amounts of chlorine, calcium, magnesium and sodium, in parts per million, by the proceedures previously outlined in this paper.

The results of these analysis may be found in the table on page 21, and by graphs at end of thesis.

The element of most importance in the regeneration of zeolite sand is sodium, due to the fact that softening is accomplished by base exchange reactions which consists of the hardness compounds, calcium and magnesium, being replaced by sodium which does not cause hardness. Therefore it is evident that we should save that portion of the rinse that contains the largest amounts of sodium. As is shown in the sodium graph, the first 16 minutes of the rinse period will give the largest amount of ? sodium. This is exactly the portion of the rinse that is being saved at the present time.

During the brining of the tank 80 gallons of saturated new brine is added to the tank. A saturated brine solution at 60 degrees F. contains theoretically 26 per cent of salt. It is coustomary to ignore solubility as affected by temperature and to assume an average solubility of 25 per cent. This solution has a specific gravity of 1.19228. One gallon of a saturated brine solution contains practically 2.479 pounds of salt. Eighty gallons of saturated salt brine would contain 198 pounds of salt of which 79 pounds is sodium.

The average concentration of sodium obtained by saving the first 16 minutes of the rinse is 6,039 parts per million. This amount of sodium is obtained during a flow of 1840 gallons, therefore there is 93 pounds of sodium in the rinse water saved.

Conclusion Drawn:-

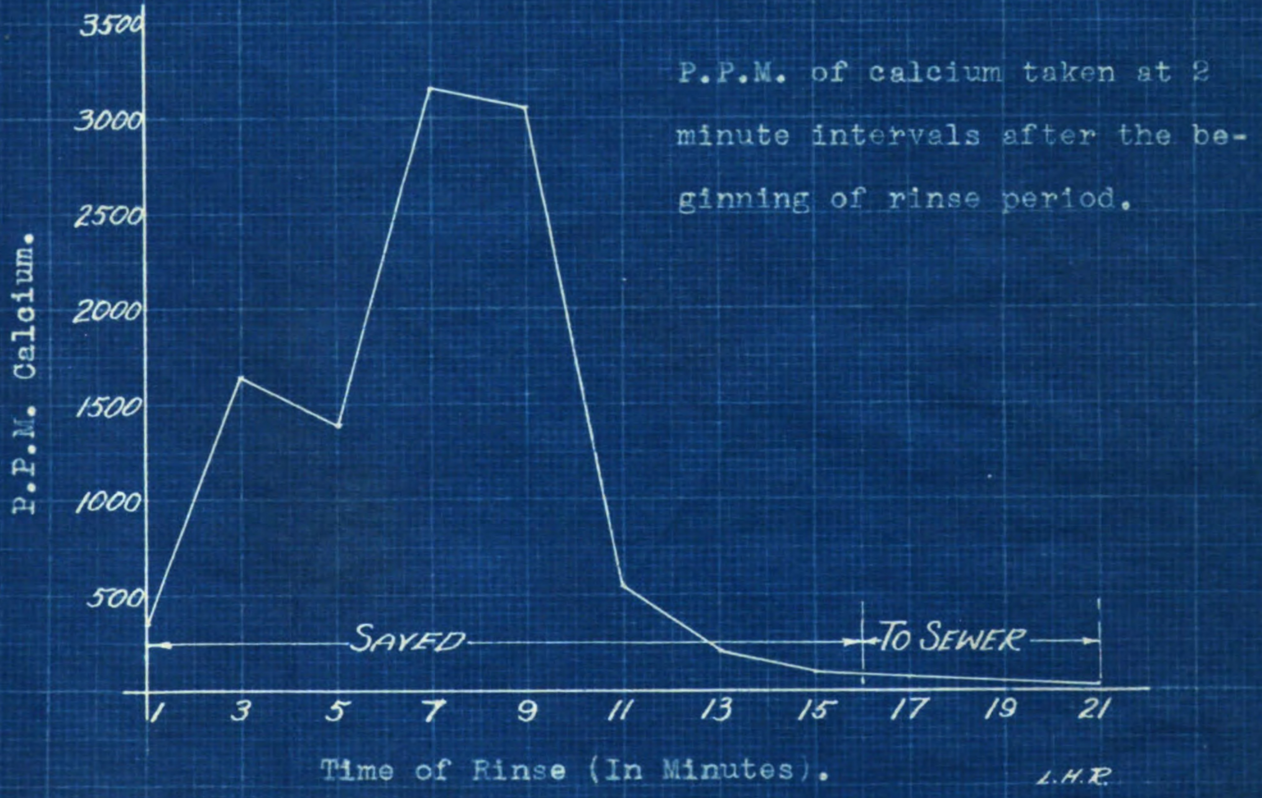
It is evident from the above results that there is some value in the use of the recovery brine, but just what this value is it is impossible to say without running more tests.

Although there is more sodium obtained from the recovery brine, than there is in the new brine that is added, the dilution is so great that it is doubtful as to its value in the regeneration of zeolite. The used brine contains 0.051 pounds of sodium per gallon while the new brine contains 0.265 pounds per gallon.

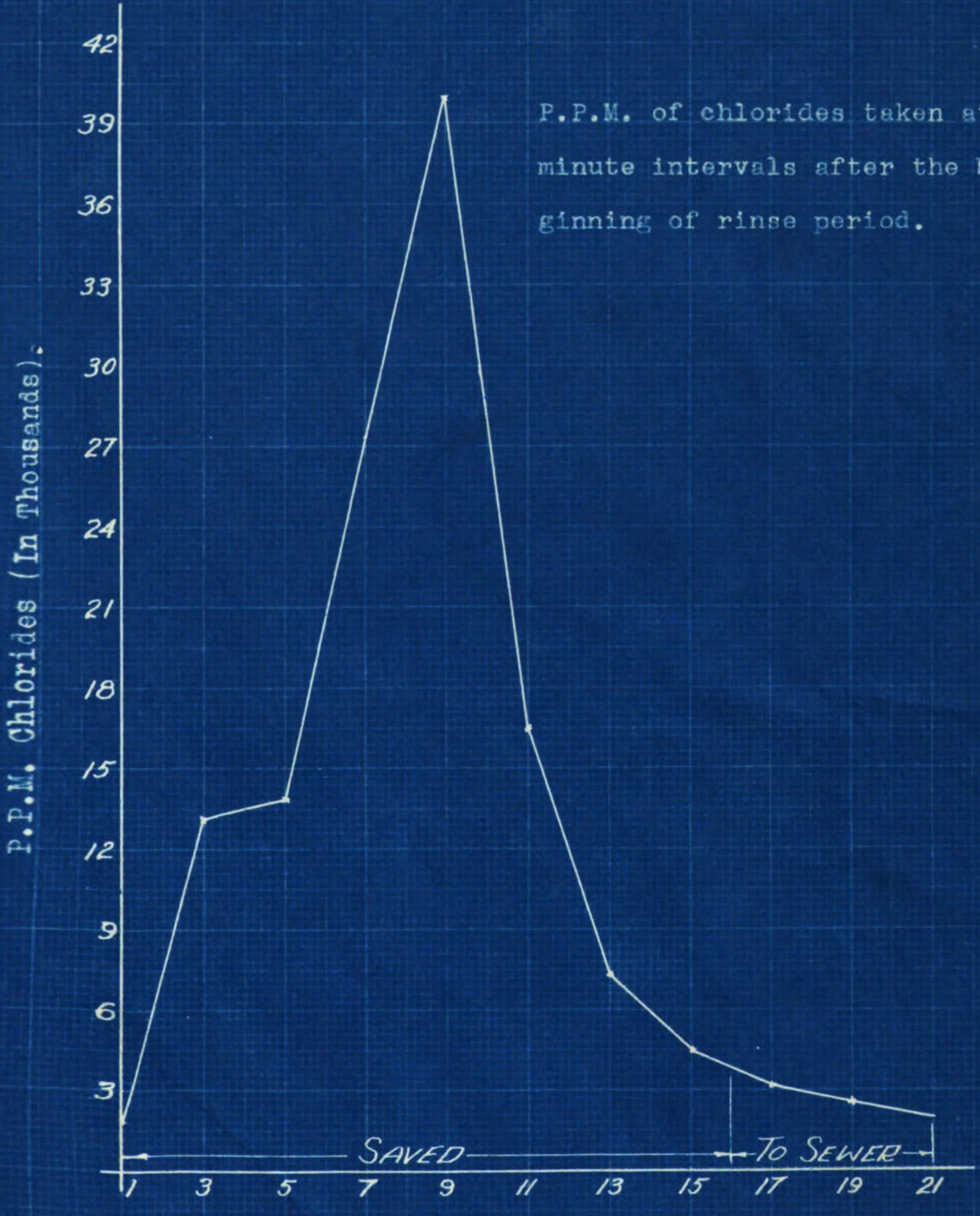
The value of the recovery brine depends upon the amount of sodium removed from it in passing through the zeolite. To determine this you would have to run the recovered brine through the sand bed without adding new brine, and then collect the brine after it has passed through the sand and re-run the analysis. This determination would be a problem in itself.

ANALYSIS OF SAMPLES

Time After Beginning of Rinse	Cholorides (p.p.m.)	Calcium (p.p.m.)	Magnesium (p.p.m.)	Sodium (p.p.m.)	Sp. Gr.
1 min.	1900	369	131	1,050	1.001
3 "	13200	1650	530	5,660	1.013
5 "	13950	1400	515	6,460	1.013
7 "	27400	3167	680	12,800	1.035
9 "	40600	3063	562	21,700	1.053
11 "	16500	548	438	9,400	1.015
13 "	7300	198	80	4,360	1.004
15 "	4400	89	35	2,680	1.003
17 "	3150	51	19	1,960	1.002
19 "	2525	33	14	1,600	1.001
21 "	1925	16	13	1,200	1.001



P.P.M. of calcium taken at 2 minute intervals after the beginning of rinse period.



P.P.M. of chlorides taken at 2 minute intervals after the beginning of rinse period.

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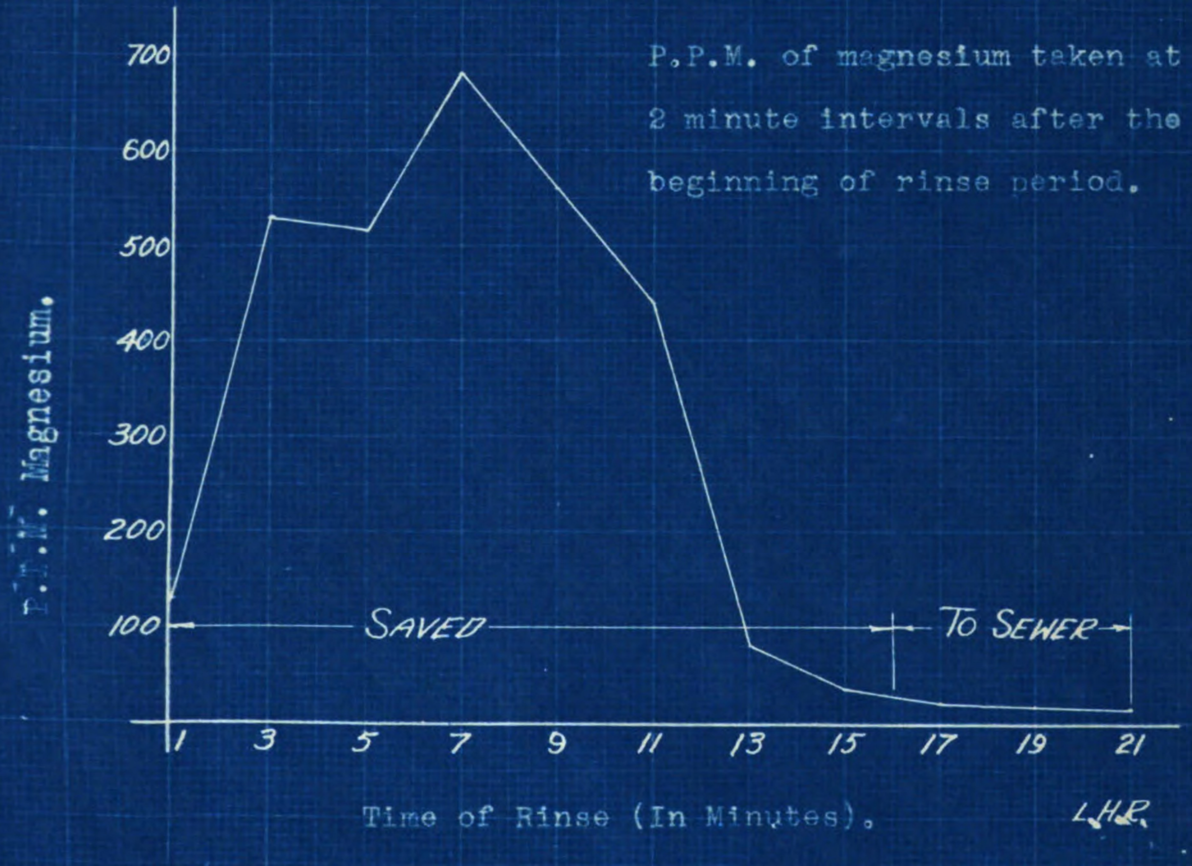
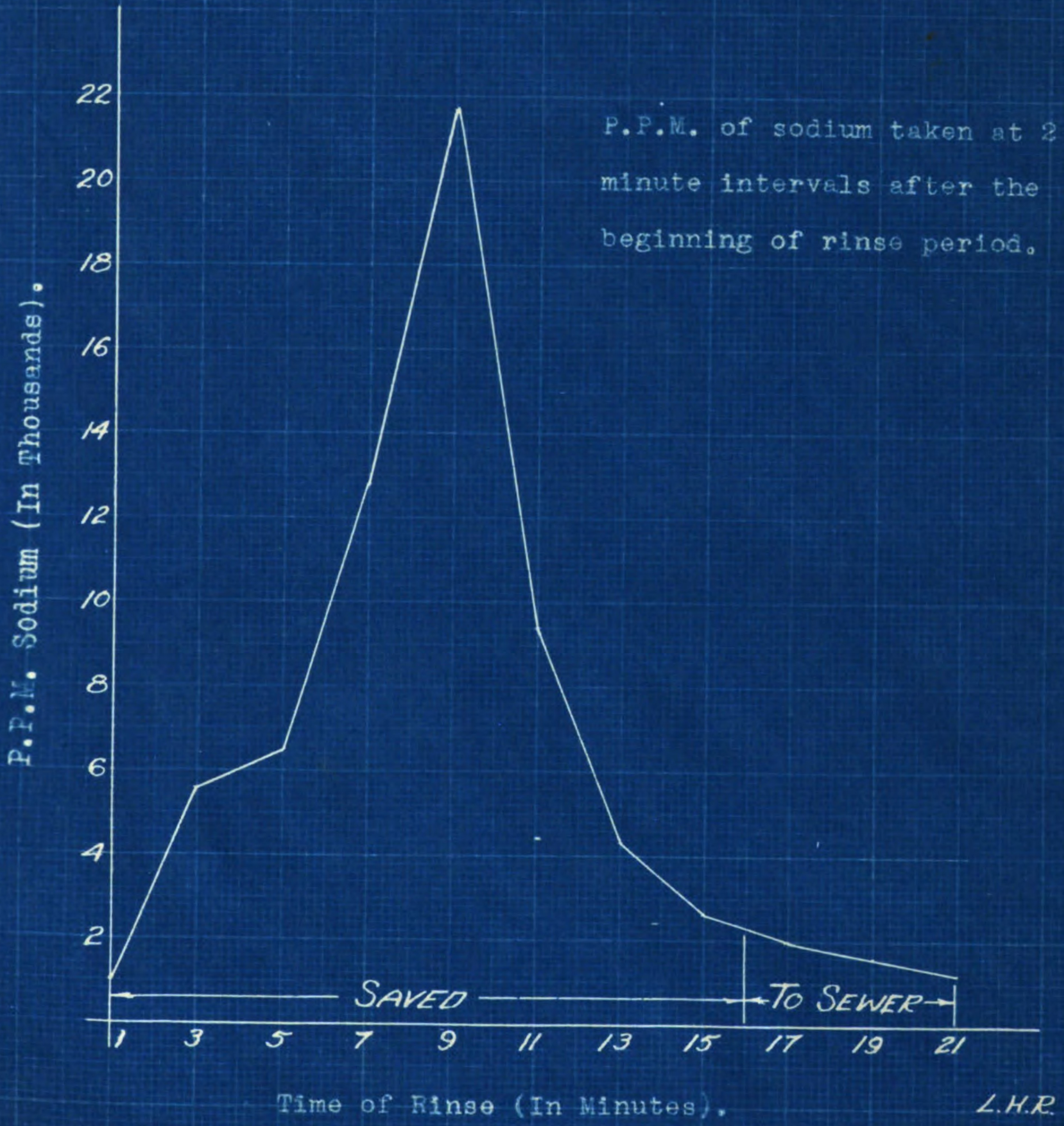


P.P.M. of magnesium taken at 2 minute intervals after the beginning of rinse period.



P.P.M. of sodium taken at 2 minute intervals after the beginning of rinse period.

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44
4
4)44 1
11 0.25
3¼
330.75
15.75
346.50

Pocket has: 4 Graphs

Graph 1