ORGANIC ION-EXCHANGE MATERIALS

BY

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Preface

This thesis is offered as partial fulfilment for the degree of Chemical Engineer at the Newark College of Engineering. It covers a very new subject — one which has been rather intensively developed by several investigators during the past three years. The writer has had the fortunate opportunity of working on organic ion-exchange materials at the Ellis-Foster Co., which kindly gave permission through Mr. Carleton Ellis for the publication of experimental results. Many thanks are due to Dr. Frank B. Root, the laboratory director, whose gracious, constructive criticisms aided the writer in all phases of the work.

An attempt has been made to present a fairly comprehensive picture of the industrial set-up in which the new materials may find application. A reasonably thorough literature search has provided what is hoped will prove an extensive bibliography. On the basis of experimental evidence presented, the properties of the materials are compared with those of the zeolites and suggestions are offered for commercial utilization.

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Introduction

The enormous industrial progress since the beginning of the twentieth century would undoubtedly not have been possible if the chemical engineering profession had been unable to keep pace with technical requirements for clean, pure water. In our daily lives we give no second thought to our abundant supply of good, safe water; but one of the paramount factors determining successful operation of almost any industrial plant is the assurance of an adequate and suitable water supply.

The necessity of such requirements has been recognized since ancient times as is witnessed by such structures as the Roman aqueducts and public baths (90)[≠]. Many methods have been discovered for rendering natural waters fit for human needs. In general, such natural waters may be classified according to source, as meteorological (rain, snow), surface (lakes, streams) and ground waters (wells, springs, etc.) (8). Each group is subject to contamination of two sorts: dissolved or suspended matter, and living organisms. The latter, although extremely important from a pathological standpoint can not be discussed in this work. The substances

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[≠] Underlined parenthetical numbers refer to numerical references in the bibliography.

in solution, especially the minerals, comprise the class with which we are concerned.

Meteorological waters are relatively pure and contain little more dissolved material than distilled water. As they collect into surface waters, small amounts of substances with which they come in contact are dissolved. It is the ground waters, however, which are most heavily laden. In percolating through the soil, ground waters absorb carbon dioxide and organic acids which tend to dissolve minerals. They are also deficient in oxygen so that certain substances which would otherwise be insoluble (e.g., iron) are held in solution. As a result, subterranean waters usually contain appreciable amounts of calcium, magnesium, iron, manganese, sodium, and potassium which occur as bicarbonates, chlorides, sulphates, and sometimes as nitrates. Ordinarily, sodium and potassium salts cause little trouble, and waters containing them may be tolerated for human consumption if they hold less than about 3000 ppm. (parts per million) sodium chloride or its equivalent (37). The calcium- and magnesium-containing waters are most obnoxious because they may not be used in laundering and kindred processes without causing the precipitation of insoluble soap curds, and because they also produce deposits of scale in tubes of steam boilers. These are situations which are obviously most undesirable and which will be discussed in further detail later (see p. 132). Such water has come to be known as "hard." It is a convention among English speaking technicians to refer to a certain number of "ppm. hardness," by which is meant that number of unit weights of calcium carbonate dissolved in a million units of pure water which would produce a water having the same soap precipitating qualities as the water in question. It is not necessary for a hard water to contain calcium ions, much less actual calcium carbonate (which actually has a very small solubility), but the hardness is expressed in terms of calcium carbonate as a matter of convenience. Waters may be loosely classified as follows (102):

Soft waters contain less than 100 ppm. total solids.
Medium hard water contains from 100 to 200 ppm. total solids.
Hard waters contain from 200 to 500 ppm. total solids.
Saline water contains 500 ppm. and over total solids.

The total solids may, as a rule, be considered as being about half calcium carbonate. Waters having a hardness of not more than 200 ppm., or not containing total solids in such quantity as to give a disagreeable taste, are satisfactory for drinking and cooking (37). An indication of the economic significance of hardness may be gained from the fact that one-tenth of a pound of soap is wasted in every thousand gallons of water for each ppm. hardness (122). It is estimated that where a municipality softens its water, there is a saving of five dollars per capita per year for every eighty ppm. hardness removed (28).

Historical and General Background

Many chemists have attempted to develop processes to remove hardness efficiently and cheaply from large volumes of water. Probably the first method was the addition of alkaline substances such as soda ash or ammonia for the purpose of softening the water. The first successful method of actually removing calcium and magnesium salts by precipitation was that of Clark who paradoxically added calcium hydroxide to remove the temporary (calcium bicarbonate) hardness (122). Porter later improved on this by adding sodium carbonate so that water containing chloride or sulphate salts could be more completely softened. This "lime-soda" process is still used in probably the majority of water treating installations today. Its chief competitor is the zeolite process.

The history of zeolites (see 10, 13, 54, 80) begins in 1756 with Cronstedt, a Swedish geologist, who so named the class of double silicate minerals because they swelled and gave off their water of hydration when heated; hence the name zeolite which means "boiling stone." J. Thomas Way (131A) discovered the base-exchange property while investigating fertilizers. He found that soils had the property of absorbing certain cations; that is, calcium was taken up and replaced by the sodium from the complex sodium-aluminum silicate (zeolite) constituent of the earths. He did not realize that the reverse reaction was also possible, namely, that the absorbed calcium was in turn replaceable by sodium. He was so convinced of the truth of his assumption that it was not possible, that he performed no experiments to determine the truth!

This discovery of the reversibility of the reaction is credited to Eichorn (54,77,80) who in 1858 showed that bases were mutually exchangeable. Neither of these early investigators forsaw the possible industrial applications of the zeolites. They suggested utilization as constituents of fertilizers, however, and Way described syntheses of zeolites by two modern processes, namely, precipitation of sodium silicate by sodium aluminate or by alum. (The first of these had really been carried out by J. N. Fuchs in 1818.)

In the period from 1896 to 1901 Harms and Rümpler (working independently) attempted to utilize zeolites industrially in the refining of beet sugar on the theory that if the potassium compounds in the sugar juices were replaced by calcium, the yield of crystallized sugars would be increased. Apparently they were unsuccessful, for base exchange silicates have never been used in sugar refining. Robert Gans was also working on this process when he conceived the idea of softening water by filtering it through a bed of the zeolites. Rümpler also claims credit for first suggesting this use, but Gans actually made, used, and patented (45) synthetic fused materials for this purpose. In 1909 the Permutit-Filter Co. of Berlin (33) was organized to exploit the Gans patents and they started to introduce and develop zeolite water softening in the United States.

The early zeolites were made by fusing materials containing alumina and silica with alkali. The resulting glassy melt was crushed, washed and graded to proper size. The action of this product was sluggish and the capacity was low; the water to be softened had to be passed through it slowly and regeneration required several hours and consumed a great excess of salt. Also, it could not supply peak loads and was especially sensitive to the carbonic acid content of the raw water.

After the introduction of the process into this country, a bentonitic clay was processed and used with somewhat better results, but this was still not very good as judged by present day standards.

By that time there were many workers in the field and the use of New Jersey greensand or glauconite was developed. This is a natural zeolite which is called "potash marl" at the mines where it is produced in Burlington County, New Jersey. The marl is dug by hand from open pits and the clay, fines, limestone, quartz, gypsum and pyrites with which it occurs are removed, and the greensand stabilized, by washing, scrubbing and varied chemical treatment (<u>23</u>). Although the base-exchange capacity is less than that of the fused synthetic zeolites, the operating capacity of a unit over a working day is greater because of the rapid regeneration period which requires only about one-half hour. There are many other advantages such as salt economy, resistance to attack by waters of low pH, cheapness, unlimited supply, etc., so that the majority of modern commercial installations are of the greensand zeolite type.

In the early 1920's, investigators began to perfect processes involving the old precipitation or "wet" syntheses (<u>15</u>,<u>132</u>). When solutions of sodium silicate and sodium aluminate or aluminum sulphate (or all three) are mixed, a gelatinous precipitate results which, on being dried to a definite moisture content and thrown into a tank of water, disintegrates into small particles of the correct size for use, and at the same time has its soluble salts washed out (105). The granules produced in this way are quite porous but are hard enough to withstand a considerable amount of abrasion in a water softening unit. This zeolite has several advantages over the greensand type among which may be mentioned a softening capacity of 2 to 8 times as great, necessity for less frequent regeneration, and higher allowable rate of flow of water through a unit. The principal disadvantage is the low resistance to aggressive water. It is coming into more general use in special applications, such as household units.

In the normal use of a zeolite, the sand-like granules are placed in a closed tank and are supported on a bed of graded sand and pebbles. The coarser pebbles lie on the bottom of the tank with progressively finer grains in the upper layers, and the zeolite rests on the topmost layer of sand. The ordinary sand prevents the zeolite from washing out. The depth of the zeolite bed is about one-half the height of the tank. The container is fitted with outlets at the top and bottom, to which are fitted a system of pipes and valves. The cycle of operation begins with the hard water being run in at the top, the tank being directly connected with the supply. It percolates downward through the base-exchange bed at a rate of about 3 to 6 gal. per sq. ft. per minute and emerges from the bottom of the tank completely softened. When the zeolite is exhausted, as determined by testing the effluent with soap solution, the downward flow is stopped and water is forced in at the bottom and out the top at a rate sufficient to suspend the granules and cause an expansion of the bed of about 50 per cent. This washes out any dirt which may have been filtered out of the raw water, and cleans each zeolite granule. Sodium chloride brine (about 5% concentration) is then run out of another tank onto the zeolite so that the bed is completely immersed. The brine is allowed to remain in the tank for 30 minutes to an hour or more, depending on the type of zeolite used, during which time the sodium replaces the calcium and magnesium in the exhausted zeolite. The mixed sodium, calcium and magnesium chlorides are then drawn off to the sewer and the water supply is again directed downward for softening, the first portion being discarded as it washes out the remainder of the spent brine.

Literature of Organic Ion-Exchange Materials

In contrast with the voluminous literature on zeolites and related inorganic base-exchange materials, references to base-exchange properties of organic substances are exceedingly sparse and isolated. This is rather unusual in view of the fact that Way's discovery (ibid.,131A) was made when working with soil, of which the humus constituents have since been shown to exhibit the phenomenon to a high degree. It is quite possible that the results of Way's original experiments were brought about by the humus in the soil as much as by the inorganic zeolite. Shortly after Eichorn's announcement of the reciprocity of the base exchange reaction, F. Rautenberg (1862) observed that forest humus exhibited this property.[≠] Heiden (1866) reported similar facts about peat and various peat preparations, which Eichorn confirmed in 1875. König (64) reviewed

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[≠] This early history follows J. F. Muller's outline (77).

the work up to 1882, determined the absorption of acids, bases, and salts by humates, and concluded that the process was chemical in nature. Six years later, Van Bemmelen showed that humic colloids formed adsorption complexes with acids, salts, and especially bases.

The study seems to have dropped from scientific interest (except for a brief but dogmatic observation in 1915 by de Dominicis (31) to the effect that soil absorbs all anions and cations) until about 1926 when Kelley and Brown (62) published a study of the relation of base exchange to soil acidity or pH. Agronomists then became concerned with this relationship and also with the problem of assimilation by plants of soil constituents as made available by base exchange of humates. There was some disagreement among authorities as to just what ingredient the base exchange should be attributed. Burgess and McGeorge (24) held that black alkali soils contain sodium aluminate and sodium silicate which form zeolite gels in soil. Sokolov (111) investigated the exchange capacity of the organic and mineral constituents of humus-bearing marl soils and attributed the high capacity exclusively to the content of parent rock. McGeorge (71) later

(1930) found that the exchange capacity of highly organic soils is approximately a linear function of the carbon content; he expressed the opinion that lignin, lignocellulose and related bodies are the active ingredients through which the reaction takes place. Mitchell (74) also reported that up to 65% of the total base exchange capacity of soil is due to organic materials. A nice compromise is found in the statement of Sigmond (110) that the most reactive part is the humus-zeolite complex which may be considered as a combination in which the anions are the humus- and zeolite-acids and the cations are the replaceable bases in the soil.

Although this property of humic acid derivatives was thus known and studied for many years, there were apparently only two commercial uses proposed. du Bellay and Houdard (32) suggested humus as an absorbent for poison gases in war time, and Fischer and Fuchs (40) observed in 1927 that water could be softened by the sodium humates from brown coal. In 1931, however, Borrowman (20) patented a process for softening water by allowing it to percolate through a granular bed of lignite, or brown coal, containing an exchangeable alkali metal until it was "more or less exhausted." The bed could be regenerated with sodium chloride brine. The process was not commercially successful because of the low exchange capacity and the disconcerting quality of "color throwing" or bleeding of a yellow or brown discoloration into the treated water. Borrowman later claimed to have overcome the color throwing by treating the lignite with sodium aluminate (21), while Tiger and Goetz (124) accomplished the same result by treatment with chromium salts.

Besides these natural humates, investigations have been made of so-called "synthetic humates" and in the last two years several patents have been granted for their applications to water softening. Natural humic acids are a chemically ill-defined class of decomposition products of plant tissue comprising humic, ulnic, crenic, and apocrenic acids (94). But none of these is a definite chemical compound. Each merely represents a type of substance with certain peculiar properties. Hence "synthetic humic acids" is an almost meaningless term and may only be defined by saying that it covers a group of substances which are acidic, amorphous, and have physical properties like those of natural humic acids. Nevertheless, there are a considerable number of references to such products in the literature in connection with soils (26,41,42,44,70,81, 87,92,113). In general, they are prepared by the destructive action of strong, concentrated acids (such as sulphuric) on vegetable products. Muller (77) conducted a research along these lines in an effort to discover the reason why the natural humus in soils carried out the exchange of bases. He treated 1 gram of various materials with 10 cc. of 80% sulphuric acid in the cold for 2 hours, diluted with 16 cc. water, and boiled under reflux for 3 hours. The base exchange capacities (expressed as milliequivalents per gram) were changed as shown in the following table:

Table I.

Substance Treated	Initial Capacity	Capacity after Treatment
Straw	0.12	1.02
Sphagnum moss	1.12	1.62
Humus	2.65	1.75
"Brown Rot"	1.07	1.09
Pure cellulose✗	0.00	1.30
Hard wood shavings	0.00	0.52

✗Treatment differed in this case in that strong sulphuric was allowed to react at spontaneously raised temperature.

Muller was interested in the problem from a scientific point of view only; he judged that he had simulated the natural decomposition processes and concluded that no definite chemical compounds were responsible for the base-exchange reaction but that rather such groups as hydroxyl (probably phenolic) and carboxyl were the controlling factors.

A process very similar to this was patented in England in 1936 (127). According to the specification, coal, lignite, or peat may be treated with concentrated sulphuric acid at a temperature below 150°C. to give a product possessing base-exchange properties. Three French patents have also appeared covering this subject. One (84) discusses the action of sulphur trioxide, sulphuric acid, zinc chloride, calcium chloride, hydrochloric acid, or phosphoric acid on coal, anthracite, sawdust, peat, lignite, starch, or molasses at temperatures from 60° to 250°C. The product is called active humus. Another (83) proposes to use about the same ingredients and temperature but carries out the reaction under pressure, calling the product "active charcoal." It was later (1937) proposed to use this material for removing small amounts of acids from liquids (85).

Perhaps the most significant and gratifying information is that disclosed in a confidential bulletin of the Permutit Co. (91) dated May 19, 1936, in which is announced the advent of the first commercial carbonaceous zeolite called "Zeo-Karb." This has been produced in limited quantities for experimental units in the plants of several large users of treated water, and practical performance records are being gathered. Aside from one or two mere mentions of the existence of the product (52,93) no information has been published about it.

Use of Synthetic Resins

The foregoing summarizes the most important literature on organic base-exchange substances with one very important exception — the paper of B. A. Adams and E. L. Holmes (3) who investigated the absorptive properties of synthetic resins.

Adams and Holmes thought that because of possible acidic properties of phenolic ("Bakelite type") resins, they might form insoluble salts with bases. They prepared a large number of such resins and found that those from monohydric phenols were soluble in alkali, and possessed the property of absorbing cations from salt solutions to only a slight degree; but formaldehyde condensation products of polyhydric phenols such as catechol, resorcinol, quinol, phloroglucinol, and the catechol tannins were insoluble in alkali and could base exchange not only with calcium and magnesium but with a wide variety of other cations. Furthermore, the action of these resins was more or less selective. For instance a tannic acid-formaldehyde product would absorb large quantities of iron; pyrocatechol-formaldehyde; antimony; and pyrogallol-formaldehyde, lead.

Certain others from phloroglucinol and quebracho tannin[≠] possessed general absorptive powers removing a wide variety of cations. The resins were capable of base exchange, and could be regenerated by dilute acids or alkali salts whose anion constituents formed soluble salts with the absorbed cations. It is evident that these are truly synthetic, organic, base-exchange materials. The experiments are described now in some detail as they formed the incentive for the work discussed in this thesis; they will later be compared with the writer's experiments.

Adams and Holmes describe the preparation of the resins as follows: "The polyhydric phenol (1 part), water (10 parts), and 40% formalin (2 parts) were heated to the boiling point and concentrated hydrochloric acid ($\frac{1}{2}$ part) was added. The resin usually

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[≠] Quebracho is a tanning agent imported in large quantities, mostly from Argentina. It is extracted from the heartwood of *Schinopsis lorentzii* and *Schinopsis balansae*. The chipped logs are digested with water containing sodium bisulphite, which increases the yield of extractives, and the solution is evaporated to dryness yielding a "sulphited quebracho extract" (51).

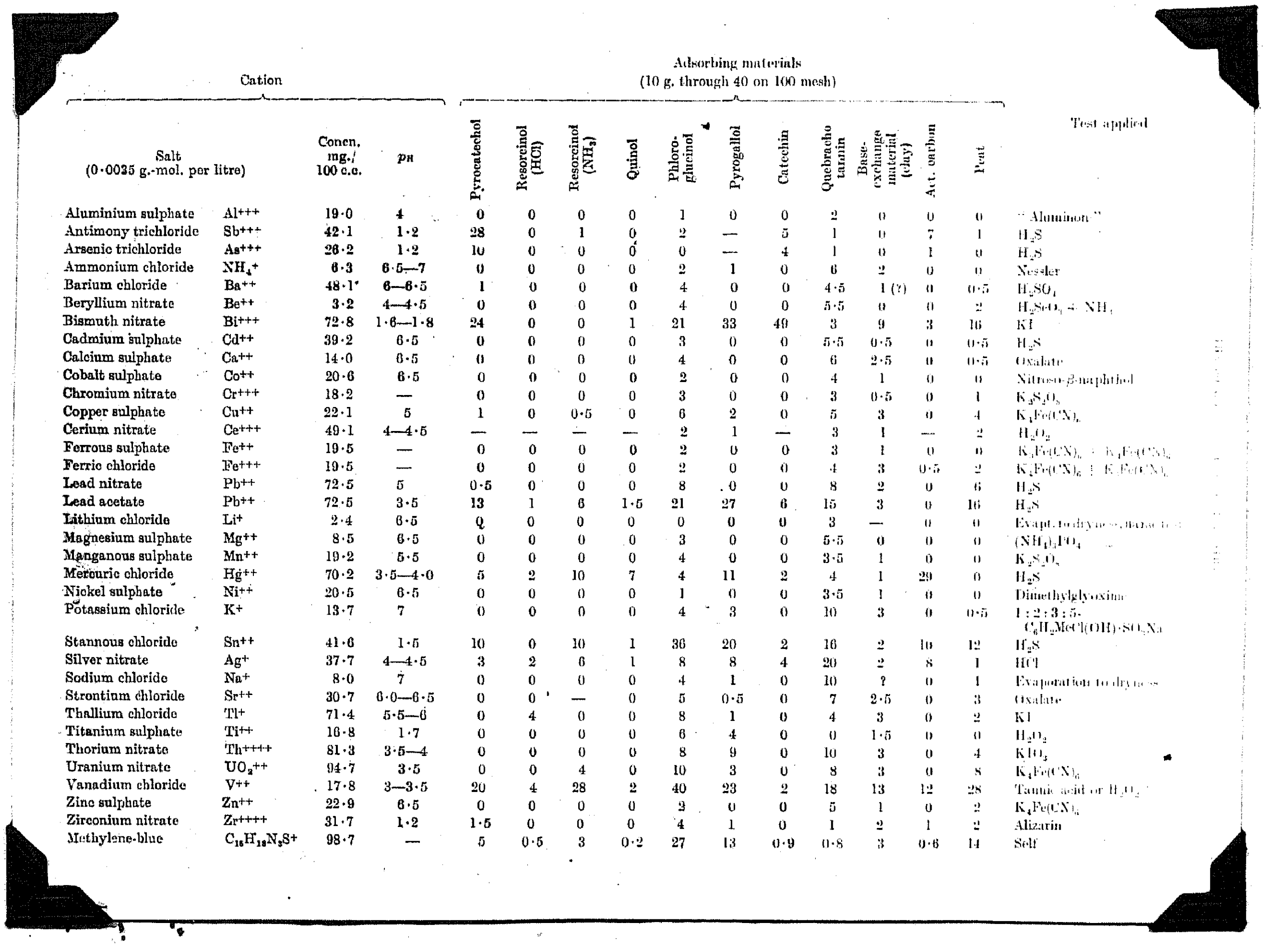
separated within a minute or two, and was filtered off and washed with alcohol and ether, and dried in vacuum. Washing could be omitted and the product dried at 25° or 100° without any perceptible change in properties. In some cases, where the reaction mixture became gelatinised, drying was carried out at temperatures up to 140° without affecting its properties. Decrease in the amount of water or employment of alcohol in the condensation favoured gelatinisation. For phenols not easily oxidised, alkalis such as caustic soda or ammonia could also be used as catalysts. With ammonia, condensation can even be carried out at room temperature. Of the catechol tannins, sulphited quebracho extract condensed readily forming a gel which dried to a very hard black mass highly suitable for use as a filter medium, and it was chosen as a typical tannin.....10 g. of the washed, dried, and sieved materials (through 40- and on 100-mesh) were placed, supported on glass wool, in perpendicular glass tubes 2 cm. diam. After treatment with 5% hydrochloric acid, the contents were washed free from chlorine ions with distilled water.

Solutions of each of the (test) salts were prepared, approximately 0.0035 gram-mol. per litre in water..... The solutions were passed through the materials at the rate of about 200 cc. per hour, and either 50 or 100 cc. of filtrate were tested for the presence of the cation...... When the beds were exhausted, that is, when cations were detectable in the filtrate, the materials were usually treated with 5% hydrochloric acid which readily removed the adsorbed cation; 5% nitric and sulphuric acids, or concentrated hydrochloric and acetic acids were also used. After washing the bed free from excess of acid it was used for subsequent experiments.

"The results are given in Table I (Table II of this thesis. See following page.) where the numbers represent the quantity in 100 cc. (i.e., numbers are 100 cc. portions—H.B.) from which at least 99% of the cations had been removed."

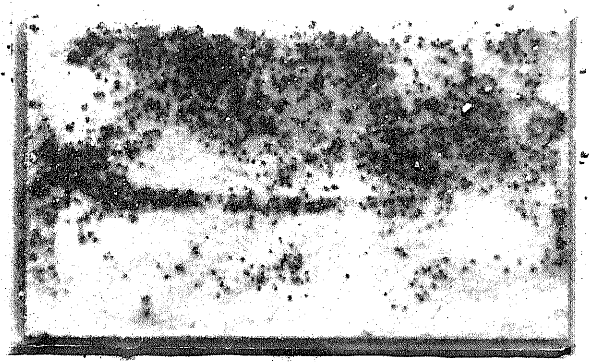
In another series of experiments described in the same paper, various tanning materials were resinified by formaldehyde and tested for water softening capacity. "The resins, set up in tubes as before, were

Table II

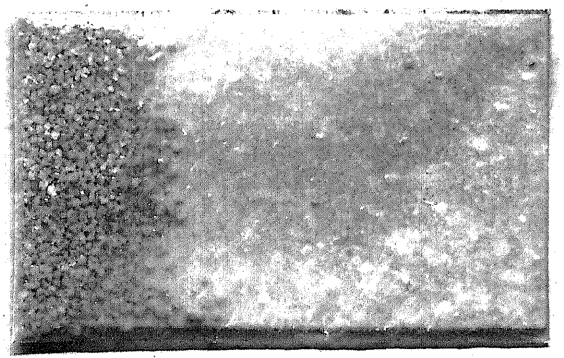


Salt (0·0035 g.-mol. per litre)	Cation	Concn. mg./100 c.c.	pH	Pyrocatechol	Resorcinol (HCl)	Resorcinol (NH_3)	Quinol	Phloro-glucinol	Pyrogallol	Catechin	Quebracho tannin	Base-exchange material (clay)	Act. carbon	Peat	Test applied
Aluminium sulphate	Al^{+++}	19·0	4	0	0	0	0	1	0	0	2	0	0	0	"Aluminon"
Antimony trichloride	Sb^{+++}	42·1	1·2	28	0	1	0	2	—	5	1	0	7	1	H_2S
Arsenic trichloride	As^{+++}	26·2	1·2	10	0	0	0	0	—	4	1	0	1	0	H_2S
Ammonium chloride	NH_4^+	6·3	6·5—7	0	0	0	0	2	1	0	6	2	0	0	Nessler
Barium chloride	Ba^{++}	48·1	6—6·5	1	0	0	0	4	0	0	4·5	1 (?)	0	0·5	H_2SO_4
Beryllium nitrate	Be^{++}	3·2	4—4·5	0	0	0	0	4	0	0	5·5	0	0	2	$H_2SeO_4 + NH_3$
Bismuth nitrate	Bi^{+++}	72·8	1·6—1·8	24	0	0	1	21	33	40	3	9	3	16	KI
Cadmium sulphate	Cd^{++}	39·2	6·5	0	0	0	0	3	0	0	5·5	0·5	0	0·5	H_2S
Calcium sulphate	Ca^{++}	14·0	6·5	0	0	0	0	4	0	0	6	2·5	0	0·5	Oxalate
Cobalt sulphate	Co^{++}	20·6	6·5	0	0	0	0	2	0	0	4	1	0	0	Nitroso-β-naphthol
Chromium nitrate	Cr^{+++}	18·2	—	0	0	0	0	3	0	0	3	0·5	0	1	$K_2S_2O_8$
Copper sulphate	Cu^{++}	22·1	5	1	0	0·5	0	6	2	0	5	3	0	4	$K_4Fe(CN)_6$
Cerium nitrate	Ce^{+++}	49·1	4—4·5	—	—	—	—	2	1	—	3	1	—	2	H_2O_2
Ferrous sulphate	Fe^{++}	19·5	—	0	0	0	0	2	0	0	3	1	0	0	$K_3Fe(CN)_6 + K_4Fe(CN)_6$
Ferric chloride	Fe^{+++}	19·5	—	0	0	0	0	2	0	0	4	3	0·5	2	$K_4Fe(CN)_6 + K_3Fe(CN)_6$
Lead nitrate	Pb^{++}	72·5	5	0·5	0	0	0	8	0	0	8	2	0	6	H_2S
Lead acetate	Pb^{++}	72·5	3·5	13	1	6	1·5	21	27	6	15	3	0	16	H_2S
Lithium chloride	Li^+	2·4	6·5	0	0	0	0	0	0	0	3	—	0	0	Evapt. to dryness, flame test
Magnesium sulphate	Mg^{++}	8·5	6·5	0	0	0	0	3	0	0	5·5	0	0	0	$(NH_4)_3PO_4$
Manganous sulphate	Mn^{++}	19·2	5·5	0	0	0	0	4	0	0	3·5	1	0	0	$K_2S_2O_8$
Mercuric chloride	Hg^{++}	70·2	3·5—4·0	5	2	10	7	4	11	2	4	1	29	0	H_2S
Nickel sulphate	Ni^{++}	20·5	6·5	0	0	0	0	1	0	0	3·5	1	0	0	Dimethylglyoxime
Potassium chloride	K^+	13·7	7	0	0	0	0	4	3	0	10	3	0	0·5	1 : 2 : 3 : 5-$C_6H_2MeCl(OH)\cdot SO_3Na$
Stannous chloride	Sn^{++}	41·6	1·5	10	0	10	1	36	20	2	16	2	10	12	H_2S
Silver nitrate	Ag^+	37·7	4—4·5	3	2	6	1	8	8	4	20	2	8	1	HCl
Sodium chloride	Na^+	8·0	7	0	0	0	0	4	1	0	10	?	0	1	Evaporation to dryness
Strontium chloride	Sr^{++}	30·7	6·0—6·5	0	0	—	0	5	0·5	0	7	2·5	0	3	Oxalate
Thallium chloride	Tl^+	71·4	5·5—6	0	4	0	0	8	1	0	4	3	0	2	KI
Titanium sulphate	Ti^{++}	16·8	1·7	0	0	0	0	6	4	0	0	1·5	0	0	H_2O_2
Thorium nitrate	Th^{++++}	81·3	3·5—4	0	0	0	0	8	9	0	10	3	0	4	KIO_3
Uranium nitrate	UO_2^{++}	94·7	3·5	0	0	4	0	10	3	0	8	3	0	8	$K_4Fe(CN)_6$
Vanadium chloride	V^{++}	17·8	3—3·5	20	4	28	2	40	23	2	18	13	12	28	Tannic acid or H_2O_2
Zinc sulphate	Zn^{++}	22·9	6·5	0	0	0	0	2	0	0	5	1	0	2	$K_4Fe(CN)_6$
Zirconium nitrate	Zr^{++++}	31·7	1·2	1·5	0	0	0	4	1	0	1	2	1	2	Alizarin
Methylene-blue	$C_{16}H_{18}N_3S^+$	98·7	—	5	0·5	3	0·2	27	13	0·9	0·8	3	0·6	14	Self

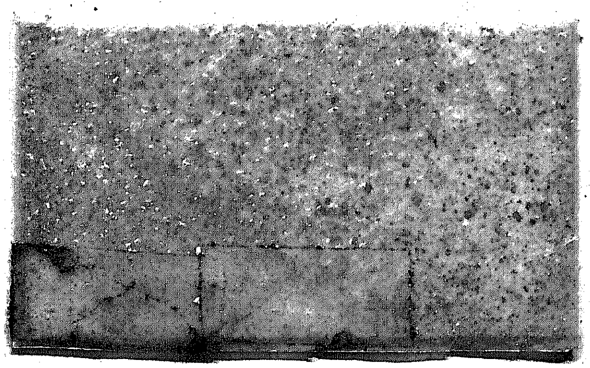
Adsorbing materials (10 g. through 40 on 100 mesh)



Greensand Zeolite



Gel Zeolite



Quebracho-Formaldehyde

Bindex-Acid Sludge

Other observations on cation exchange may be briefly summarized as follows: It is unlikely that the adsorptive properties were caused by inorganic impurities because the resins (except those from tannins) gave no ash on incineration. (Quebracho tannin resin had a 2% ash.) Regarding the materials tested in the first series of experiments, "The filtrates from the base-exchange material (treated clay (117)) always contained iron, aluminum, and silica. The powdered peat had a pronounced solubility, particularly in concentrated hydrochloric acid, and after twenty successive experiments, less than 50% remained in the tube. It was always difficult to remove the excess of regenerating acid from the activated carbon bed."

Cation absorption capacity was considerably increased if the pH of the raw water was high (more alkaline).

Dried gaseous ammonia was absorbed by resorcinol resin which also had bactericidal properties.

This thesis is primarily concerned only with base exchange. Nevertheless, an important innovation in the science of water treatment was discussed in the paper being reviewed. It is so intimately connected with base exchange that its inclusion here is not felt to be misplaced.

The success that attended Adams and Holmes with their experiments led them to believe that basic resins might be efficacious for removing anions from solution. They suggest that such a material might be chosen from aldehydic condensation products of (1) aromatic bases, (2) amides, and (3) proteins, but they investigated only the first class. They found that aniline and m-phenylenediamine, condensed and dried in the presence of an excess of hydrochloric acid, formed black, hard masses insoluble in water, alcohol or acetone. "10 g. of the dried gels, ground and sieved through 40- and on 100-mesh, were placed in tubes as in previous experiments and washed first with N-ammonia solution and then with water until free from any excess of ammonia. It was found that any alkali, including carbonates and bicarbonates, was suitable for activating these resins providing that a soluble salt was formed with the anion.

"A solution of sulphuric acid containing 34 mg. per 100 cc. was passed through the resins and the acid was removed from .... 900 cc. by the black aniline resin and from 2100 cc. by the m-phenylenediamine resin.

"Washing the resin beds with 100 cc. of N-ammonia solution and then 100 cc. of water removed the sulphuric acid, but with water washing alone, little, if any, sulphate ions were removed..... From dilute aqueous solutions, nitric, hydrochloric, and acetic acids as well as phenol were removed by these resins. A solution of calcium sulphate was passed through a black aniline resin which had been treated with aqueous hydrochloric acid and washed free from excess of acid. The filtrate was found to contain the whole of the calcium as chloride, but no sulphate ions were detectable. This is an example of anion exchange analogous to cation exchange."

Adams and Holmes indicated that they would publish a subsequent account of further experiments but this has not been forthcoming. They have, of course, patented their invention (4) but the specifications disclose very little more information than is given in the original article. Their work has aroused much interest in the chemical world, and it has been reviewed or abstracted by several individuals (5,76,79).

A rather diligent search of the literature by the writer yielded no other references to the anion-exchange reaction as mentioned in the last quoted paragraph above, except for a few notations of the occurrence of anion exchange in soils (128). In the Fall of 1937 a patent was granted to Kirkpatrick (63) for a quebracho-formaldehyde product almost identical to that of Adams and Holmes. The United States patents of Adams and Holmes were issued in January, 1938.

Report of Original Experiments

Experiments were carried out by the writer at the Ellis-Foster Co. laboratories (See Figure 1) over the period from August, 1936, to September, 1937. The work of Adams and Holmes (3) was first repeated, but attention was later shifted to the development of new types of base-exchange media which may be called "acid

Fig. 1 General View of Laboratory

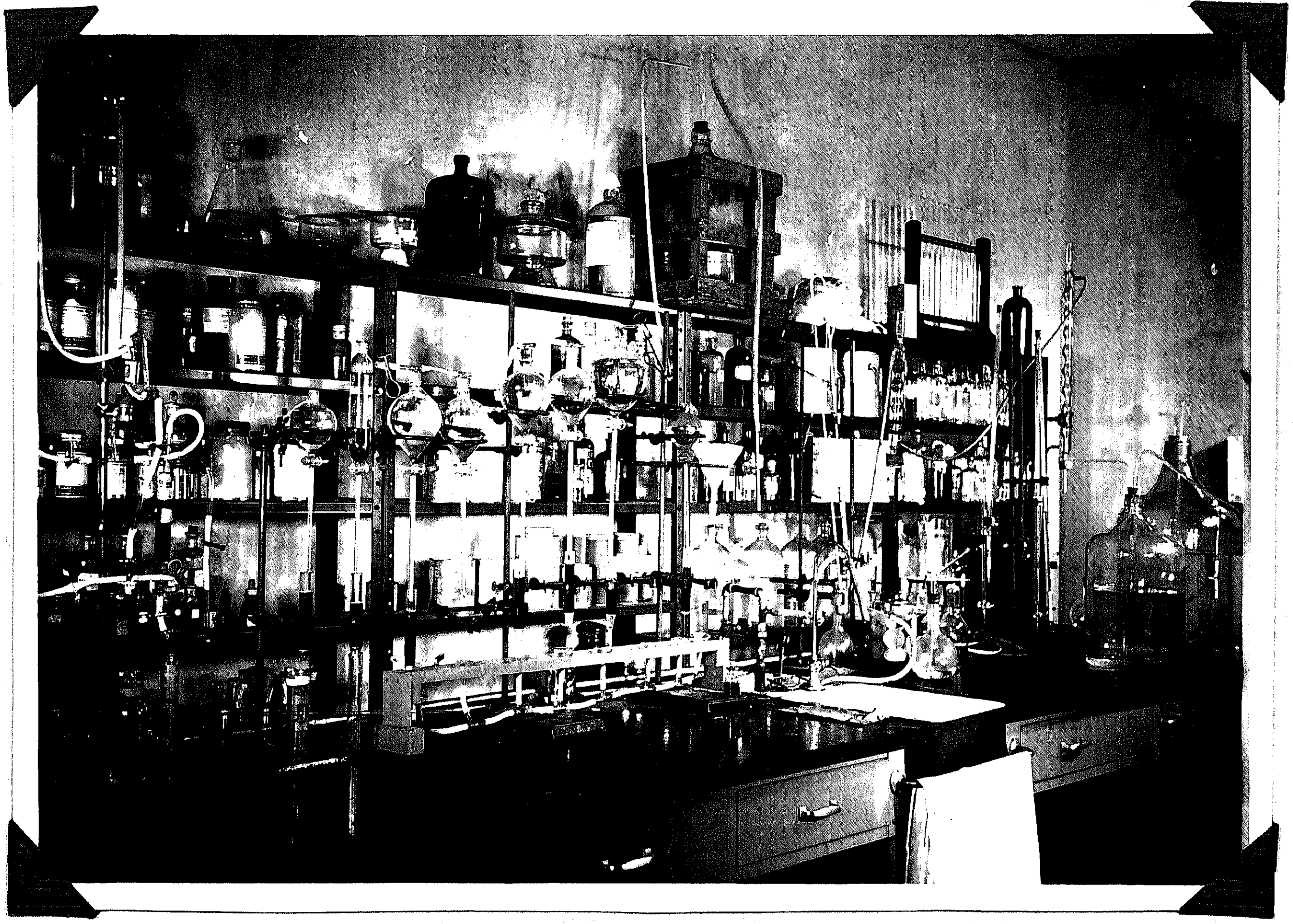
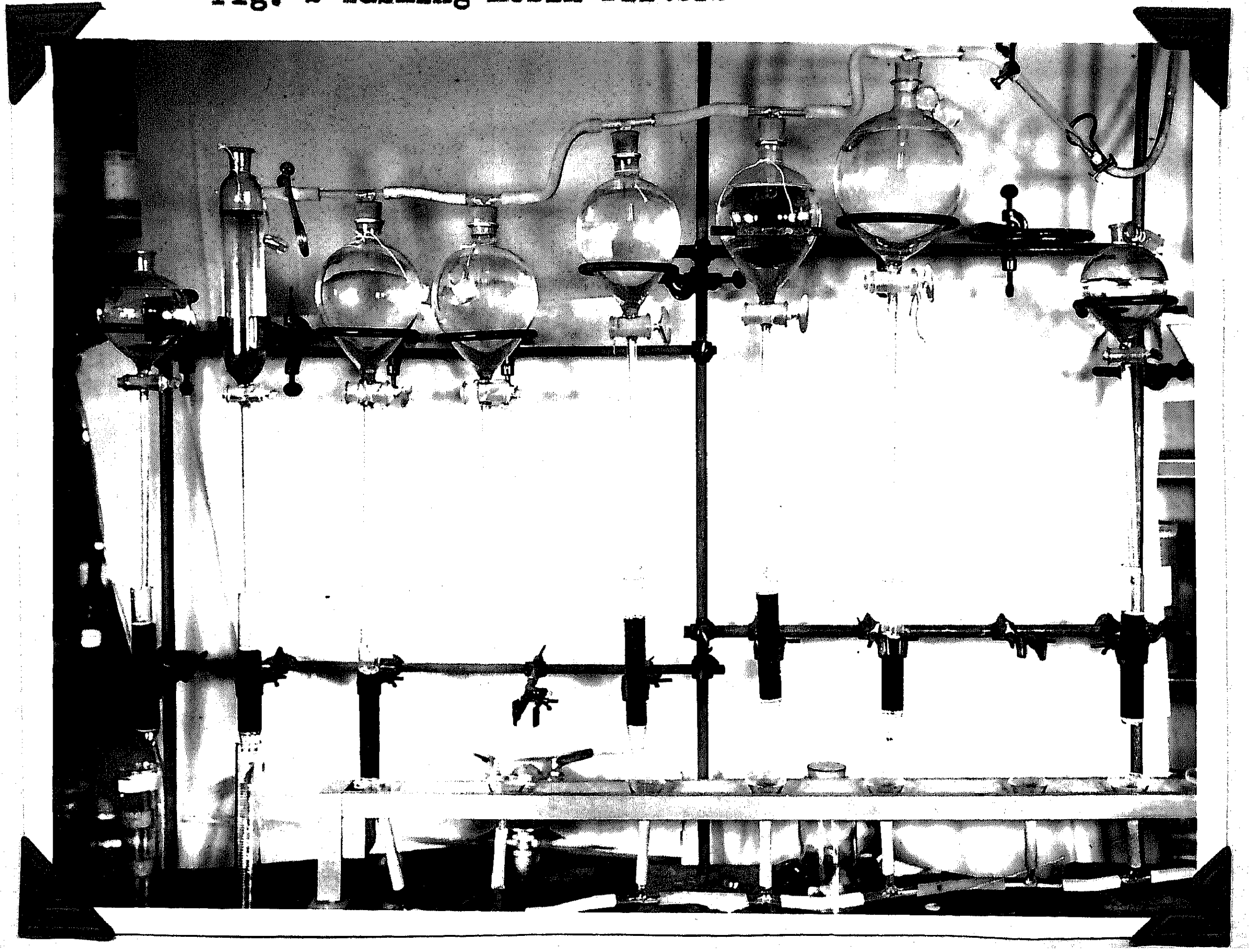


Fig. 2 Washing Resin Filters



resinoids" to distinguish them from synthetic resin organolites. The reported experiments were selected as being typical; they have been arranged and numbered as indicated in the outline on the following page. This was done to group related experiments together, to show such relation by experiment number, to reduce the space and time required for recording procedures, to eliminate needless repetition, and to provide an easy reference system for calling attention to experimental data in the other sections of the thesis. No discussion of results or conclusions are included because these topics can be more logically treated in appropriate places in the body of the thesis.

Schematic Outline of Original Experiments

I. Water Softening Materials (Calcium and Magnesium Removal)

  A. Aldehyde Resins

    1. Quebracho-Formaldehyde

    2. Other Phenol-Formaldehyde Resins

    3. Other Aldehydes

  B. Acid Resinoids

    1. Sulfuric Acid

    2. Acid-Sludge (from petroleum refining)

    3. Other Acids

  C. Sundry Resins

  D. Zeolites

II. Removal of Other Cations from Solutions

  A. Gold

  B. Others

III. Removal of Anions from Solutions

  A. Amine Resins

  B. Acid-Regenerated Materials

  C. Fluoride Removal

  D. Amphoteric Resins

IV. Semi-Commercial Tests

A. Preparation of High Base-Exchange Resins

B. Determination of Characteristics

General Methods

Determination of Ion-Exchange Capacity

It was desirable to use a method of determining exchange capacity which would combine the following features:

1. Be applicable to both anion- and cation-exchange.
2. Provide laboratory data which might be applied to possible operating conditions with reasonable accuracy.
3. Require a minimum of time per determination.
4. Require a minimum of base-exchange material.
5. Require a minimum of "impure water" for testing.

The literature gives several methods applicable to zeolites which have been used by various investigators. Probably the simplest is that mentioned by Muller (77) and modified recently by Ferguson, Musgrave, and Patton (38), wherein a weighed amount of a finely powdered sodium-regenerated material is placed in contact with an excess of another (say calcium) ion for a definite period. The unabsorbed ion is determined by some convenient analytical method and that absorbed calculated by difference. This method, however, gives the ultimate base-exchange value which is no criterion of operating value (123) and hence does not satisfy condition 2 above.

The most recent and probably most reliable method is that given by Hoover (53) in the Report of the Committee on Tentative Methods for Testing Zeolites. This procedure requires for convenient operation large equipment such as tanks for preparing test waters, multiport valves, large tubes for containing materials to be tested, etc. Although it undoubtedly reproduces operating conditions quite faithfully, it is unsuited for a small laboratory in which several widely varied investigations are going on simultaneously. The method used by Bird (17) was decided upon as most nearly meeting the requirements. It was slightly modified and used as described below.

The base-exchange materials were ground, usually with a mortar and pestle, and screened through 20-mesh on 40-mesh screens. The classified material was given a preliminary washing by decantation with distilled water to remove colloidal and semi-colloidal fines, and the wet slurry was poured with excess water into a glass tube 2 cm. in diameter to form a settled and drained column 10 cm. high. The glass tubes were constricted at one end to about 1.5 cm. in diameter and into this cone-shaped section was fitted a 2 cm. diam. perforated porcelain plate. A very thin asbestos mat was placed on the plate in the manner ordinarily used in preparing a Gooch crucible except that suction was not used. This supported the column of material to be tested on top of which was placed another perforated porcelain plate which served to distribute the inflowing water, thus minimizing channeling.

The prepared filter bed was further washed by allowing distilled water to drip through from a separatory funnel (see Figure 2, p. 31). It was then tested by allowing a solution containing a known quantity of a given ion to flow through from a dropping funnel, usually at the rate of about 200 cc. per hour. The effluent was collected in 50 cc. portions and was analyzed for the constituents sought to be removed. When a positive test was found in the effluent, the column was regenerated by allowing a suitable solution to flow through, followed by a flushing with distilled water, or the test was discontinued. From the volume of material used (31.4 cc.) and the volume of water treated, the capacities can be calculated.

The "impure" waters used were prepared by dissolving appropriate substances in Montclair tap water. The average concentrations used were as follows, but specific strengths are noted in each experiment:

Hardness (calcium): A solution of calcium sulphate or chloride containing 400 ppm. hardness as calcium carbonate.

Chloride: Hydrochloric acid containing 0.25 mg. chloride ion per cc.

Fluoride: Sodium fluoride dissolved to make 10 ppm. fluoride ion.

Lead: 1 mg. lead acetate per cc.

Gold: 1 mg. gold chloride per cc.

Bicarbonate: Sodium bicarbonate solution containing 1 mg. bicarbonate ion per cc.

It should be noted that Tiger (123) lists 18 variables to be considered in a zeolite-quality determination and that the Permutit Co. requires data on even more on their laboratory report sheets. Obviously the effect of each on all of the many materials prepared was impossible to determine. Nevertheless, it is felt that the above method (with several supplemental tests described in those particular experiments using them) has given representative and comparative data.

Analytical Methods

The analytical methods used throughout the research have been gathered together for easy reference and to avoid repetition. Unless otherwise stated in the reports of experiments it is to be assumed that these procedures have been followed.

Hardness (calcium ion) was determined by the usual method of titrating with alcoholic soap solution according to Scott ("Standard Methods of Analysis," 2nd Edit., Revised, p.559). This is stated to be accurate to 10 ppm.

Chloride ion was tested for by the method of Volhard, i.e., titration with silver nitrate using potassium chromate as an indicator.

Bicarbonate ion was titrated with 0.1 N hydrochloric acid using methyl orange. By test, 1 mg. bicarbonate ion could be detected in 100 cc.

Fluoride was determined by the colorimetric method of Sanchis (106). This involves forming a red Zirconium-Alizarin lake, the color of which progressively changes to yellow on addition of fluoride ion. Nessler tubes are used for comparison with standards.

Lead was detected qualitatively with ammonium sulfide.

Gold was qualitatively tested by the development of Cassius Purple with stannous chloride or by producing a characteristic blue or green color (depending on pH) with benzidine acetate. The latter was found more sensitive.

Aluminum was qualitatively determined by using "aluminon" (67) (aurin tricarboxylic acid). A positive test was indicated by development of a deep red flocculent precipitate in the presence of aluminum ions.

Nickel, of course, was tested for with dimethylglyoxime.

Uranium in the form of uranyl ions (UO_2) gives a deep red precipitate with ferrocyanide (69, p. 289).

Zinc was shown to be present by using a modification of the usual volumetric determination (69, p. 106). The color of potassium uranyl ferrocyanide was destroyed in the presence of dissolved zinc by virtue of formation of zinc ferrocyanide.

Experiments

IA1a

Following the procedure outlined by Adams and Holmes (3), 200 g. solid sulphited quebracho extract, 400 g. 37% formaldehyde and 1 liter of water were heated to boiling and 100 cc. concentrated hydrochloric acid were added. The entire mass instantly gelled, swelled, and broke the flask.

In order to moderate the reaction so as to delay gelation for a few seconds in order that the acid catalyst might be mixed in uniformly to produce a homogeneous gel, 100 g. of quebracho were dissolved in 1 liter of water and 200 g. 37% formaldehyde, and the solution was heated to boiling. Concentrated hydrochloric acid, 50 cc., diluted with 150 cc. water, was added with rapid stirring and the mass set to a soft gel which was broken up, washed with water, and filtered off.

It was thought that it might be possible to use the wet gel as a filtering medium, but when this was tried, the filter bed cohered and packed down so that water would pass through at only a very slow rate. Therefore, the product was dried at 50° C. until a black, hard, brittle material was obtained.

It was tested with a solution of calcium sulphate containing 400 ppm. hardness (as calcium carbonate) as described in the General Method. The effluent was acid (the action of the acid catalyst being equivalent to regenerating with an acid) so it was neutralized with 0.1 N alkali, using bromthymol blue (color change at pH 7) as indicator, before titrating with standard soap solution. A total of 350 cc. of the hard water were softened. The next 50 cc. portion contained 95.7 ppm. hardness.

The filter bed was regenerated with 400 cc. of 5% sodium chloride. It was again tested with 400 ppm. water, this time 450 cc. being softened. Another sample of the material softened the same amount.

When regenerated with 300 cc. of 10% sodium chloride, a column tested an average of 700 cc. of 400 ppm. water.

IA1b

The procedure of IA1a was repeated using 50 cc. of concentrated ammonium hydroxide instead of the hydrochloric acid as a catalyst. No reaction seemed to take place, so 100 cc. more ammonia were added. The solution was boiled for 1 hour under reflux but no precipitate formed. Evidently ammonia does not catalyze the gel-producing reaction.

IA1c

100 g. quebracho extract were dissolved in 300 g. water over a steam bath. The solution was cooled to room temperature and 200 g. of 37% formaldehyde and 50 cc. concentrated hydrochloric acid were added.

After standing about 2 minutes, the mass gelled with syneresis and a slight exothermic reaction. The gel was dried at 86° C. in vacuo. The product was such a fine powder that it could not be satisfactorily screened and it packed too tightly to allow water to drip through a bed of it.

IA2a

100 g. sym-xylenols, 500 g. water and 200 g. 37% formaldehyde were heated to boiling, 50 g. concentrated hydrochloric acid were added and the solution boiled for 1 hour under reflux. A cream colored resin separated which was filtered off, washed and dehydrated at 110° C.

The material would not soften any water of 400 ppm. hardness.

It was thought that possibly the resin retained a sufficiently acidic nature so that an alkaline hard water might be softened. To this end, a solution of calcium hydroxide containing 700 ppm. hardness was used. None was softened, however.

IA2b

50 g. gallic acid, 500 g. water, 100 g. 37% formaldehyde, and 25 g. concentrated hydrochloric acid were boiled under reflux for ½ hour. The precipitate was filtered off, washed, and dried at 86° C. in vacuo. The product was a light fluffy powder which could not be used as a filter bed. It was densified by cementing with cellulose acetate solution in dioxan. It could then be ground and screened, but the material would not soften water.

A similar resin was prepared using tannic acid instead of gallic. This was also a light powder which behaved identically with the gallic acid product.

The materials were treated with 5% sodium chloride solution, but they remained inert.

IA2c

200 g. 37% formaldehyde, 100 g. logwood extract (solid) and 1000 g. water were heated to boiling and 50 cc. hydrochloric acid were added. After refluxing for 2 hours, the resin was filtered off and dried.

It was tested with calcium sulphate solution of 400 ppm. hardness, but none was softened. After regenerating with 5% sodium chloride solution, 200 cc. of the water were softened.

A product produced in the same way from hematine (oxidized logwood) would not absorb any calcium even on "activation" with sodium chloride.

IA2d

100 g. of fustic crystals were dissolved in 300 g. water over a steam bath to form a very cloudy solution. This was boiled with 200 g. 37% formaldehyde and when 50 cc. of concentrated hydrochloric acid were added, the whole quickly gelled. The washed precipitate was dried at 86° C. in vacuo.

It was tested with calcium sulphate solution of 400 ppm. hardness but none was softened. After treating with 5% sodium chloride solution, however, 400 cc. of the water were softened.

The procedure was repeated with chestnut extract, cutch, and gambier in turn, but the materials would not soften any water even after treatment with sodium chloride.

IA2e

About 3 pounds of the stems and leaves of the Poison Ivy plant (Rhus toxicodendron), the toxic constituent of which is a phenol, were placed in 10 liters of 5% sodium hydroxide and brought to a boil. The mixture was allowed to stand overnight when the extract, a very dark brown liquid, was filtered off. Preliminary tests with diluted extract showed development of a dark green color with acidified ferric chloride; absence of precipitate by boiling the alkaline solution with formaldehyde; and a voluminous, flocculent precipitate by boiling with acidified formaldehyde.

On the basis of these preliminary experiments, the whole of the extract was acidified with hydrochloric acid and boiled with 8 liters of 37% formaldehyde. The gel-like precipitate was filtered off and dried at 86° C. in vacuo.

The resin would not absorb either calcium or magnesium from solutions containing about 400 ppm. hardness.

A similar material prepared from Sicily sumac was also devoid of water softening properties.

IA3a

A resorcinol-furfural resin was prepared by reacting 100 g. resorcinol dissolved in 200 g. isopropyl alcohol with 100 g. furfural in the presence of 20 cc. of concentrated hydrochloric acid. A violent exothermic reaction occurred yielding a vesiculated black gel which was dried at 86° C. in vacuo.

The product would not soften any water even after treatment with 5% sodium chloride.

Equally inert products were obtained following the procedure but using quebracho (in water solution instead of alcohol), or aniline instead of resorcinol.

IA3b

50 g. quebracho extract were dissolved in 500 cc. water and 100 g. acetaldehyde and 50 cc. concentrated hydrochloric acid were added. The solution was boiled under reflux for 30 minutes when a hard resin had separated. This was filtered off, washed, and dried

at 50° C.

It was tested with a calcium sulphate solution containing 406 ppm. hardness, 250 cc. being softened. After regeneration with 200 cc. of 10% sodium chloride brine, 500 cc. were softened.

A similar product, prepared by using butyraldehyde instead of acetaldehyde, would not base-exchange with calcium.

IA3c

100 g. quebracho extract were heated to boiling in 200 g. acetone under reflux. 50 cc. concentrated hydrochloric acid were slowly added. The solution was refluxed for 10 hours with no precipitation of resin. The solution was poured into 2 liters of water when a precipitate came down. This was filtered off and dried at 50° C.

When tested with calcium sulphate solution of 407 ppm. hardness, 200 cc. were softened. The filter bed was regenerated with 200 cc. of 10% sodium chloride solution, but upon washing with distilled water, the column disintegrated and clogged.

IBla

100 g. sulphited quebracho extract powder were stirred into 300 g. of concentrated sulphuric acid (sp. gr. 1.83). The mixture (which spontaneously heated, became black, and evolved sulphur dioxide) was allowed to reach its equilibrium temperature spontaneously in one case, and in other experiments the reaction mixture was either cooled or heated to obtain the desired temperature. Batches were made at 50°, 80° (spontaneous temperature), 100°, 125°, and 150° C., these temperatures being maintained for 10 minutes and the reaction mixtures being allowed to stand for 20 minutes more while gradually cooling somewhat. The mixture was poured into a large volume of water, and the precipitate filtered off, washed, dried, and ground to pass through 20 over 40 mesh screens. A series of 3 trials was made on each material with 400 ppm. hard water, i.e., each was tried initially and then regenerated twice with 200 cc. of 10% sodium chloride and tried after each regeneration.

The results of the series is given in the following table:

Table IV.

Temperature of Reaction	Yield in Grams	Cc. Water Softened at 400 Ppm. Hardness
50° C.	55	1450
80° C.	80	1650
100° C.	155	1050
125° C.	128	700
150° C.	124	750

IB1b

The procedure of IB1a was repeated, using 100 g. chestnut extract and 300 g. sulphuric acid, at 25°, 60°, 93° (spontaneous temperature), 120°, and 150° C. The exchange capacities are expressed as the volume of 400 ppm. hard water softened per 31.4 cc. column of organolite.

Table V.

Temp. of Reaction	Cc. Water Softened	Yield in Grams
25° C.	400	
60° C.	350	75
93° C.	600	93
120° C.	500	88
150° C.	550	

IB1c

100 g. of chestnut extract were mixed with varying proportions of concentrated sulphuric acid, and the

mixes were allowed to spontaneously reach thermal equilibrium. After 30 minutes, the batches were poured into large volumes of water, filtered, washed and dried. The spontaneous temperatures reached, yields, weights acid used, and capacities are recorded:

Table VI.

G. Sulphuric Acid	Spontaneous Temp.	Yield in Grams	Cc. Water at 450 Ppm. Softened
100	123	86	250
200	99	96	350
300	93	93	550
400	83	118	800
500	68	120	700
600	75° (heated)	155	400

IBld

100 g. ground cutch were stirred into 300 g. concentrated sulphuric acid and allowed to stand for 1 hour. The black product was poured into a large volume of water and the precipitate was filtered off, washed, and dried.

The material softened 850 cc. of water at 400 ppm. hardness. After regeneration with 400 cc. of 10% sodium chloride, 750 cc. were softened. When regenerated again with 200 cc. of 5% hydrochloric acid, 1000 cc. were softened.

The procedure was repeated using hematine instead of cutch, but the product would not absorb any calcium ions (cf. IA2c).

IB1e

A sample of liquid waste hemlock cellulose sulphite liquor was evaporated to dryness on a hot plate. 100 g. of the solid product were added to 300 g. of concentrated sulphuric acid, and the temperature spontaneously rose to 75° C. After standing ½ hour it was dumped into a large volume of water, filtered off, and dried. The product softened 700 cc. of water containing 478 ppm. hardness.

The experiment was repeated using a waste poplar cellulose sulphite liquor. This material softened 850 cc. of the water. See also IB2c.

IB1f

50 g. of pine sawdust were stirred into 300 g. of sulphuric acid and allowed to stand for ½ hour to

reach its thermal equilibrium. The black material was filtered off and dried at 110° C. A total of 400 cc. of 456 ppm. hard water was softened, and after regeneration with 200 cc. of 10% sodium chloride, 350 cc. were softened.

Another sample of the same sawdust was heated below the kindling temperature until it was charred to a dark brown. This material was devoid of base-exchange properties.

A redwood flour-sulphuric acid product softened 950 cc. of 435 ppm. hard water. Again, a charred (heated) redwood material showed no base-exchange properties.

Using alpha-flock in place of the pine sawdust (a commercial powdered wood pulp from which most of the soluble matter had been extracted with dilute caustic) only 150 cc. of 435 ppm. hard water were treated.

IBlg.

Following the procedure of IBlf, the following materials were treated with sulphuric acid with the resulting noted exchange capacities (expressed as cc. of 400 ppm. water softened).

Table VII.

Ingredient	Initial Trial	After First Regeneration
1. Bran	0	0
2. Peanut shells	0	50
3. Dead oak leaves	0	0
4. Hemlock Needles		800
5. Ground chestnut bark		600
6. Chestnut sawdust		600
7. Peat	950	900
8. Anthracite	0	0
9. Gum acroides	100	100

IBlh

Samples of "Columbia" activated carbon and of activated coconut carbon were tested and found to soften no water.

The coconut activated carbon was treated with sulphuric acid as in the preceding experiments but no base-exchange capacity was developed.

100 g. of cane sugar were stirred into 200 g. of sulphuric acid and allowed to stand for 10 minutes. The product was a hard vesiculated mass which was washed in water and dried at 55°C. This absorbed calcium from 100 cc. of water of 400 ppm. hardness; after regeneration with 250 cc. of 10% sodium chloride, 150 cc. of water were softened.

IB2a

50 g. of chestnut extract and 300 g. of water soluble sludge (sulphonic acids) from a white oil treating plant were mixed together and allowed to stand for 1 hour. The product when poured into a large volume of water was completely water soluble.

The experiment was repeated using 100 g. chestnut extract and 300 g. sludge, and heating the mixture slowly to 150° C. The material gradually became more viscous and finally resembled a wet granular solid. It was washed with a large volume of water and dried. The product softened an average of 750 cc. of 478 ppm. hard water.

When allowed to stand for 1 hour in contact with distilled water, no color, taste or odor was detectable in the supernatant water.

IB2b

A series of experiments analogous to IB1a was run, using 100 g. quebracho extract and 500 g. acid sludge. The temperatures at which the various batches were run is recorded below with the yields and base-exchange capacities.

Table VIII.

Temperature, ° C.	Yield, Grams	Cc. Water Softened at 400 Ppm. Hardness
50	0	(Product water soluble)
80	243	1650
100	207	350
125	327	350

IB2c

100 g. of powdered, dried, hemlock sulphite liquor (marketed under the trade name "Bindex") and 400 g. acid sludge were heated to 80° C. for 10 minutes, allowed to stand ½ hour, diluted to 2 liters with

water, filtered, and dried at 110° C. This product softened an average of 1250 cc. of water of 478 ppm. hardness (equivalent to 1500 cc. of 400 ppm.), using 250 cc. of 10% sodium chloride as regenerant.

A product made by substituting concentrated sulphuric acid for the sludge softened 1300 cc. of 400 ppm. water.

IB2d

50 g. peat were stirred into 250 g. warmed acid sludge. The mix was heated at 110° C. for 10 minutes, allowed to stand 20 minutes more, and poured into a large volume of water. The product was largely water soluble. A small amount of precipitate was filtered off and dried. The material softened 350 cc. of water containing 422 ppm. hardness.

IB2e

Samples of chestnut extract and quebracho extract were heated at 150° C. and hemlock sulphite liquor at 300° C. until they became infusible, i.e., they first melted and then solidified on further heating. All three materials remained water soluble.

A portion of the acid sludge was heated at 100° C. for 1 hour. It remained completely water soluble.

IB3a

50 g. quebracho extract were stirred into 200 g. of 85% orthophosphoric acid and allowed to stand 18 hours. The mix was poured into a large volume of water when a slight precipitate appeared, the majority of the reaction mixture being water soluble. The precipitate was filtered off, washed, and dried. The product softened an average of 500 cc. of 456 ppm. hard water using 200 cc. portions of 10% sodium chloride for regenerating.

The experiment was repeated, using redwood flour instead of quebracho. In this case the product softened 650 cc. of the hard water.

IB3b

100 g. quebracho extract and 150 g. phosphoric anhydride were stirred together. A violent reaction

took place with much spontaneous heating. The product was a black granular mass which was poured into a large volume of water, washed, filtered and dried. The finished material softened 250 cc. of water at 400 ppm. hardness.

IB3c

50 g. redwood flour were digested in 400 cc. of concentrated hydrochloric acid for 3 days. The mixture was diluted, filtered and dried. The product was not capable of calcium absorption.

IB3d

100 g. concentrated nitric and 400 g. sulphuric acid were mixed and cooled, and about 10 g. of quebracho extract were added. An extremely violent reaction took place, the temperature rose to 100° C., the froth filled a 2-liter beaker, and dense fumes of nitric oxide were given off.

In an attempt to moderate the reaction, 100 g. quebracho extract and 300 g. of sulphuric acid were mixed and allowed to stand for 30 minutes. Then 80 g.

of nitric acid were slowly added. The reaction was again violent, the temperature rising to 130° C. and nitric oxide being evolved. The mixture was allowed to stand until cool when it was dumped into a large volume of water and the precipitate filtered off and dried. The product softened only 100 cc. of 478 ppm. hard water.

IB3e

100 g. chromium trioxide were dissolved in 400 g. water. A violent exothermic reaction occurred when a small amount of chestnut extract was added.

The experiment was repeated, dissolving 100 g. chromium trioxide in 1 liter of water and placing the solution in a running-water cooling bath. 50 g. of chestnut extract were added gradually, keeping the temperature below 25° C. The mix was allowed to stand ½ hour, diluted, filtered and dried at 110° C. The product would not soften any water even after treatment with 10% sodium chloride.

IB3f

100 g. chestnut extract and 200 g. sodium bisulphate were mixed and heated at 150° C. for 2 hours. The product was a black vesiculated, brittle mass which had no water softening properties.

IB3g

200 g. fluosilicic acid (30% H_2SiF_6) were mixed with 50 g. chestnut extract. No reaction seemed to occur, so the mixture was heated to 50° C. and a precipitate settled out. After standing one hour, this was filtered off, washed and dried. It would not absorb calcium ions.

The experiment was repeated, boiling the reactants under reflux for 20 minutes. The precipitate which formed was filtered off, washed, and dried and found to soften 100 cc. of water containing 383 ppm. hardness after regeneration with 200 cc. 10% sodium chloride.

IB3h

110 g. ethyl alcohol and 200 g. concentrated sulphuric acid were mixed and 150 g. chestnut extract were added. The mix was allowed to stand for one hour, then dumped in a large volume of water, filtered, washed, and dried. A column of the material softened only 50 cc. of 456 ppm. hard water.

150 g. of concentrated sulphuric acid and 150 g. oleum (65% SO_3) were placed in a flask fitted with an air condenser and 150 g. benzene were added in small portions. After all the benzene was in, the benzene sulphonic acid was heated a short time and allowed to cool. 100 g. chestnut extract were added, allowed to stand one hour, washed, filtered, and dried. The product did not soften hard water.

IC1a

An alkyd resin was prepared by heating together 23 g. glycerol, 38 g. triethanolamine, 25 g. tung oil acids, and 86 g. phthalic anhydride. At 230° C. the material gelled. The product was ground and baked at 120° C. for 16 hours. It swelled when placed in water.

Another resin was made by heating 46 g. glycerol, 74.5 g. triethanolamine, and 222 g. phthalic anhydride to 210° C. when the mixture gelled. The cold, hard, brittle gel was ground and placed in the customary glass tube. On washing with distilled water, the flow gradually diminished and finally ceased. The resin had swelled to a coherent, hard, tough mass allowing no passage of water; it was too water sensitive.

A gel made as in the preceding paragraph was heated for 90 minutes at 230° C. in an oil bath. This was sufficiently water resistant to allow a test with calcium chloride solution (containing the equivalent of 200 ppm. calcium carbonate). Neither calcium nor chloride ions were absorbed. After treatment with 200 cc. 5% sodium carbonate, the resin swelled.

IC1b

25 g. tung oil acids, 24 g. glycerol, and 61 g. phthalic anhydride were heated to 240° C. when the mix started to gel. Ordinary seashore sand was quickly

dumped in and mixed with the gel. The mixture was spread out on a hot plate at 150° C. (exposed to the air) for 2 hours and baked over night in an oven at 120° C. This produced grains of sand coated quite uniformly (as examined under a microscope) with alkyd resin. The granules were tested by the general method but would not absorb calcium, chloride, or bicarbonate ions.

IC2a

A thoroughly cured (highly polymerized) urea resin was prepared as follows: 50 g. urea, 134 g. 37% formaldehyde, and 5 cc. of 40% sodium hydroxide were mixed and allowed to stand for 10 minutes when 40 cc. of 10% hydrochloric acid were added. The solution was quickly poured into a shallow dish where it soon set to an opaque, white, hard gel. The ground, washed product did not absorb calcium or bicarbonate ions.

IC2b

Monomethylolurea was polymerized by allowing it to stand in cold 15% hydrochloric acid over night. It was then dried at 50° C. The product was identical with that of IC2a.

IC3a

A light colored grade of rosin was ground, screened, and tested. No calcium was removed from calcium sulphate solution. No bicarbonate ion was absorbed from a sodium bicarbonate solution.

IC3b

200 g. rosin were melted at 160° C. and 60 g. maleic acid were gradually added. (The two react by the Diene Synthesis. See 35, Chapter 40.) The temperature was taken to 200° C. and the product allowed to cool. A column of the material was treated with sodium hydroxide solution, when it partly dissolved and disintegrated. After washing, it was tested with calcium sulphate, but none was softened.

IC3c

Gum acroides, unmodified and also reacted with formaldehyde and with sulphur did not soften water or absorb bicarbonate ions.

IDla

Commercial greensand zeolite or glauconite (trade marked "Zeodur" by the Permutit Co.) and synthetic or gel zeolite ("Decalso" of the Permutit Co.) were tested by the general method using calcium sulphate solution containing 340 ppm. hardness (as $CaCO_3$). The Zeodur softened 900 cc. of the water and the Decalso softened 4400 cc.

See also IVBla.

IIAla

The resin prepared from poison ivy (IA2e) was tested for capacity to absorb dissolved gold. A solution containing 1 g. auric chloride per liter was dripped through the filter of resin over a period of two months, 15,750 cc. passing through. The effluent was continuously tested for gold ions, but with negative results. At the end of the period the column was passing solution very slowly (less than 100 cc. per day) having almost clogged.

Attempts were made to recover the gold from the resin by leaching with distilled water, 5% acetic acid, 5% hydrochloric acid, 1% sodium carbonate, 1% sodium hypochlorite, aqua regia, and bromine water in turn, but none removed any gold. When a dilute potassium cyanide solution was dripped through, no gold was found in the effluent; however, on digesting the resin in potassium cyanide solution exposed to the air for three days, a majority of the gold was extracted.

The leached resin was washed with dilute hydrochloric acid and distilled water and used again with gold chloride solution, this time absorbing 5,800 cc.

The absorbed gold could also be recovered by igniting the resin, but this, of course, precluded further use.

IIA2a

A number of other materials were tested with following results (expressed as cc. of gold chloride solution treated):

Table IX.

Material	Exp. No.	Cc. Treated
1. Gallic-Formaldehyde	IA2b	0
2. Polymerized monomethylolurea	IC2b	250
3. Xylenol-Formaldehyde	IA2a	0
4. Sumac-Formaldehyde	IA2e	150
5. Lead-Quebracho-Formaldehyde	IIIB1b	11,550
6. Chestnut-Sulphuric (93° C.)	IB1b	†

IIA3a

Since certain materials possessed a high gold-absorptive capacity, a new technique was developed. The materials were very finely powdered and one gram was kept suspended for 15 minutes by vigorous mechanical stirring in 500 cc. of gold chloride solution containing 0.5 g. per liter. The solid was then filtered off and the gold was found to have been substantially completely removed from the solution. By prolonging the suspension period to 30 minutes, the amount of powdered absorbent could be reduced one-half.

Those substances found applicable are:

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†Qualitative test showed high absorptive power; experiment was not run until column was completely saturated.

Material	Experiment No.
1. Quebracho-Formaldehyde	IA1a
2. Quebracho-Acid Sludge	IB2b
3. Gallic Acid-Formaldehyde	IA2b
4. Tannic Acid-Formaldehyde	IA2b
5. Sumac-Formaldehyde	IA2e
6. Quebracho-Formaldehyde	IA1c
7. Quebracho-Phosphoric Anhydride	IB3b
8. Chestnut Sawdust-Sulphuric Acid	IB1f
9. Quebracho-Acetaldehyde	IA3b
10. Poplar Sulphite Liquor-Sulphuric	IB1e
11. Chestnut Extract-Sulphuric (93°)	IB1b

Those found to remove little or no gold are:

Material	Experiment No.
1. Xylenol-Formaldehyde	IA2a
2. Synthetic gel zeolite (Decalso)	ID1a
3. Willow charcoal	----

The gold was recoverable from the filtered suspended matter by the method of IIA1a, i.e., by digestion with cyanide.

IIA3b

The possible interfering effect on gold absorption by other ions was investigated.

Using 1 g. of the quebracho-acid sludge material (IB2b) in 500 cc. of 0.05% gold chloride solution, the addition of 1 g. calcium chloride or 2 g. sodium chloride to the solution was without effect on the ability to extract gold. When the powdered absorbent was digested in 5% calcium chloride solution for 1 hour (i.e., the calcium base-exchange material was formed) it still removed auric ions.

The addition of 1 g. sodium cyanide prevented complete absorption, however. This was overcome by adjusting the pH of the solution to 4.0 with sulphuric acid.

IIA4a

A sample of waste water from gold pen point nib manufacture (furnished by the Parker Pen Co.) provided a practical test of gold extraction methods. The water contained a light colored sediment and some colloidal material, and had an odor of cyanide, a pH of 8.5, and a gold content of 0.02 mg. per cc. A portion of the water was passed through a column of quebracho-formaldehyde resin (IA1a). About one-half of the gold content was absorbed.

By using the method of IIA3a and adjusting the pH to 4 (See IIA3b), the gold was completely removed.

IIB1a

A column of poison ivy resin (IA2e) was tested with a solution of 1.32 g. lead acetate trihydrate in 1 liter of water. 500 cc. were passed through, the effluent showing negative tests for lead with ammonium sulphide. This did not saturate the column (being in the nature of a qualitative test). It was regenerated with 10% acetic acid (the lead appearing in the acid effluent) and it again absorbed more lead.

Filters of gel zeolite (ID1a) and of chestnut-sulphuric acid material (IB1b) also absorbed lead from lead acetate solutions.

IIB2a

The method of IIA3a was tested on zinc chloride, uranyl chloride, nickel sulphate, and lead acetate, using quebracho-acid sludge material (IB2b). None of the cations were absorbed.

IIIA1a

50 g. m-phenylenediamine were dissolved in 150 cc. conc. hydrochloric acid diluted with 500 cc. of water. 150 g. of 37% formaldehyde were added. The gel was washed with water, drained and dried at 86° C. in vacuo.

The dried material swelled and became soft when placed in water, but it hardened and became insoluble when washed with 5% sodium carbonate. It was tested with sodium bicarbonate solution but no bicarbonate ion was absorbed. After washing with distilled water the material was tested with dilute hydrochloric acid (containing 0.28 mg. chloride ion per cc.), and the chloride ion was removed from 200 cc. The column was regenerated with 1% sodium hydroxide and tried again with bicarbonate but none was absorbed even after treatment with 5% acetic acid.

IIIA1b

50 g. m-phenylenediamine were dissolved in 300 g. of water and 150 g. of 37% formaldehyde containing 25 cc. 40% sodium hydroxide were added. In a few

seconds a sticky violet-brown colored precipitate came down which coagulated and rapidly hardened. The material was air dried. It would not absorb bicarbonate ions and removed chloride only partially from 200 cc. of test water.

IIIA1c

100 g. aniline, 200 g. 37% formaldehyde, and 25 cc. 40% sodium hydroxide were placed in a flask, an almost immediate, exothermic resinification taking place. The mix was boiled under reflux for ½ hour, and the white insoluble resin was washed and dried at 50° C. It did not remove bicarbonate ions and dissolved in the chloride test solution.

IIIA2a

8.5 g. p-aminophenol, 100 g. water, 25 g. 37% formaldehyde, and 10 cc. concentrated hydrochloric acid were heated under reflux for 7 hours. On standing over night a small amount of sticky resin settled out which was dried at 86° C. in vacuo. The product was soluble in water.

IIIA2b

25 g. m-aminophenol were dissolved in 50 cc. concentrated hydrochloric acid diluted with 200 g. water, and 150 g. 37% formaldehyde were added. The whole immediately set to a gel which was heated for 30 minutes on a steam bath, washed, and dried.

A column of the material was washed with 250 cc. of 5% sodium carbonate followed with distilled water and then tried with dilute hydrochloric acid containing 0.224 mg. chloride ion per cc. The chloride was 91% removed from 600 cc. of the solution. After regenerating with 250 g. of 8.8% sodium sulphate solution it was tested with a solution of calcium chloride containing 327 ppm. hardness and 0.442 mg. chloride ion per cc. There was a slight diminution of chloride content but no calcium absorption. The filter was regenerated with 5% sodium carbonate and again tried with the dilute hydrochloric. Although the acidity was neutralized, no chloride ion was absorbed. This was followed by 2 successive regenerations with 250 cc. of 5% sulphuric acid after which the chloride was 91% removed from 600 cc. and then 80% from 350 cc. A final regeneration with 5% sodium carbonate dissolved the material slightly and it would remove no more chloride.

IIIA3a

Following Beilstein (III, 676), aniline black was prepared, dissolving 20 g. potassium chlorate, 16 g. ammonium chloride, 30 g. copper sulphate and 40 g. aniline hydrochloride in 500 cc. water and heating to 60° C. A slight precipitate was obtained. After standing 2 hours, it was filtered off, washed and dried at 110° C. The yield was about 10 g. The material disintegrated when placed in water and hence a filter-bed could not be made.

IIIA3b

50 g. aniline were dissolved in dilute sulphuric acid and 100 g. sodium dichromate dissolved in water

were gradually added with constant cooling in running water. The thick black precipitate was filtered off, washed and dried at 110° C. The yield was 113 g.

This material removed 98.5% of the chloride from 2000 cc. of a solution of hydrochloric acid containing 0.25 mg. chloride ion per cc. The column was regenerated with 250 cc. of 8.8% sodium sulphate and it then removed 99% from 1300 cc. After regeneration with 250 cc. of 5% sodium carbonate, only 100 cc. were dechlorinated; but following a treatment with 250 cc. of 4% sodium hydroxide, 80% of the chloride was removed from 1500 cc. A second regeneration with sodium hydroxide provided a 78% removal from 900 cc.

IIIA3c

The procedure of IIIA3b was repeated using 100 g. potassium permanganate as the oxidizing agent. The product removed 80% of the chloride from 1050 cc. of the test solution. After 2 successive regenerations with 250 cc. of 5% sodium carbonate, 150 cc. were 75% dechlorinated and 600 cc., 50%.

IIIA3d

Using potassium chlorate as in IIIA3b, a material was obtained which would not absorb chloride and which dissolved and disintegrated to the extent of 75% when treated with 5% sodium carbonate.

IIIA3e

An attempt was made to oxidize aniline by blowing air through a solution of aniline sulphate containing a trace of copper sulphate and heated on a steam bath for 90 hours. Only a negligible precipitate formed.

IIIA4a

The procedure of IIIA3b was repeated, replacing the aniline with xylidine. The product disintegrated badly when placed in water. It did not remove chloride after each of the successive regenerations with 5% sodium carbonate, 8.8% sodium sulphate, 5% sulphuric acid, and 4% sodium hydroxide.

IIIA4b

IIIA4a was repeated using phenetidine, toluidine, phenylhydrazine, and naphthylamine. All of the materials removed a negligible amount, or none at all, of chloride ions.

IIIA5a

50 g. dried egg albumin were dissolved in water and 200 g. 37% formaldehyde were added. The solution was boiled and the gelatinous precipitate so formed was dried at 86° C. in vacuo. The product softened and swelled when placed in water and was hence not suited for a filter-bed.

IIIA5b

20 g. zein, 20 g. urea and 100 g. 37% formaldehyde were heated to boiling and then dried in vacuo at 86° C. The product was tested with sodium bicarbonate solution but no bicarbonate ion was absorbed.

IIIA5c

50 g. casein were slowly added to 200 g. 37% formaldehyde containing 10 g. sodium hydroxide. The thick mass was dried at 86° C. in vacuo; the product swelled in water.

IIIA5d

100 g. dried blood were boiled for 10 minutes with 500 g. water, 300 g. 37% formaldehyde, and 50 cc. concentrated hydrochloric acid. The precipitate was filtered off, washed and dried. The product removed neither bicarbonate nor chloride.

See also IC2a and -b, IC3a and -c, and IIID2a.

IIIB1a

A solution of calcium bicarbonate was prepared by adding an excess of calcium carbonate to tap water and bubbling carbon dioxide through the suspension for several hours. The resulting solution was filtered and diluted so as to contain 400 ppm. hardness and 0.473 mg. bicarbonate ion per cc. Various materials were regenerated with 250 cc. of 5% sulphuric acid and tested with the water of temporary hardness. The water was softened and the bicarbonate content was destroyed by virtue of the hydrogen ions exchanging for the calcium ions. The results are expressed as cc. of water softened and debicarbonated:

Table X.

Material	Exp. No.	1st Run	2nd Run
Acid Sludge-Sulphite Liquor	IB2c	1500	1900
Oak Leaves-Sulphuric Acid	1B1g	1250	1650
Quebracho-Formaldehyde	1A1a	450	500
Quebracho-Sulphuric Acid (80° C.)	1B1a	1800	

See also IB1d for another case of acid regeneration.

IIIB1b

A filter of acid sludge-hemlock sulphite liquor base-exchange material (IB2c) was regenerated with 250 cc. of 5% sulphuric acid and tested with a solution of sodium bicarbonate containing 0.96 mg. bicarbonate ion per cc. The bicarbonate of 900 cc. was destroyed.

IIIB1c

A column of the acid sludge-hemlock sulphite liquor material (IB2c) was regenerated with 250 cc. of a 10% solution containing equivalent quantities of sodium chloride (i.e., 13.6 g.) and sulphuric acid (11.4 g.). The test solution contained 356 ppm. hardness and 0.415 mg. bicarbonate ions per cc. The calcium was absorbed from 2300 cc. of the water but the bicarbonate was removed from only 1100 cc. Starting with the 1150th cc. portion the bicarbonate content gradually increased to 70% of the raw water in the last portions, although the water up to 2300 cc. was soft.

IIIB1d

A 50 cc. portion of the effluent from treatment by acid sludge-sulphite liquor material in Experiment IIIB1a was titrated with 0.0937 N potassium hydroxide. To reach the methyl orange end point, 0.3 cc. were required, while 1.0 cc. more were used to the phenolphthalein end point. A second portion was boiled for 15 minutes and titrated as before. This time 0.2 cc.

were required to the methyl orange and only 0.1 cc. more to the phenolphthalein.

IIIC1a

The following materials were tested for fluoride removal with a tap water solution of sodium fluoride containing 10 ppm. fluoride ion. No appreciable amount of fluoride was absorbed by any of them, in spite of regenerating successively with sodium hydroxide, carbonate, chloride, and sulphate, and sulphuric acid.

Material	Experiment No.
1. m-Phenylenediamine-Formaldehyde	IIIA1b
2. Aniline Black	IIIA3b
3. Quebracho-Sulphuric Acid	IB1a
4. Synthetic gel zeolite (Decalso) saturated with manganous chloride	
5. Synthetic gel zeolite (Decalso) saturated with calcium chloride	

IIID1a

100 g. aniline hydrochloride and 100 g. phenol dissolved in 500 g. water, and 400 g. 37% formaldehyde were mixed together, the whole setting to a soft red gel within a few seconds. The gel was broken up, 100

cc. of concentrated hydrochloric acid were added and the reaction mixture was further boiled under reflux for 10 minutes. The gel hardened to a brick red, brittle mass which was washed and dried at 86° C. in vacuo. The product was tested with a solution of calcium chloride, but the water was neither softened nor was chloride removed.

IIID2a

100 g. bone oil (American Agricultural Chemical Co.) and 500 g. formaldehyde were boiled under reflux for 30 minutes, but no reaction seemed to take place. 50 cc. of concentrated hydrochloric acid were added through the condenser. An exothermic reaction took place and after boiling for 5 minutes a gel separated which was washed and dried at 110° C.

The product was tested with a calcium chloride solution but neither ion was removed. After regeneration with 250 cc. of sodium hydroxide, the chloride ion was 75% eliminated from a hydrochloric acid solution containing 0.224 mg. chloride ion per cc.

See also IIIA2b and IC1a and -b.

IVAla

A 9-pound (4 kilogram) bottle of 66.5° Be. sulphuric acid was emptied into a 10-quart kettle and 1500 g. powdered sulphited quebracho extract were gradually added while stirring. The temperature threatened to rise above 75° C. when about 1/3 of the quebracho had been added, but this was easily controlled by placing the kettle in a cold water bath for a few minutes. The temperature remained at 73-75° C. for the remainder of the time. After standing 30 minutes the product, a black pasty mass, was dumped into about 4 gallons of water, allowed to stand for 1 hour and drained off on a wire screen. It was further washed by playing a stream of water over it while on the screen, and dried at 60° C. The yield was 1822 g., 121% on the quebracho input or 33.2% on the total weight input.

The base-exchange capacity was 1350 cc. of water of 400 ppm. hardness, using 250 cc. 10% sodium chloride for regenerating.

IVA1b

The procedure of the preceding experiment was repeated using 2 kilograms acid sludge from white oil refining and 500 g. quebracho extract. It was necessary to apply heat to keep the temperature at 75° C.

The yield was 820 g., equivalent to 164% on the quebracho or 32.7% on the total input. The base-exchange capacity was 1450 cc. of 400 ppm. hard water.

IVA2a

A semi-plant scale apparatus was set up (see Figures 3, 4, and 5) consisting of a 2 cu. ft. jacketed kettle equipped with stirrer and exhaust blower; a ceramic vacuum filter with a 30 mesh wire cloth strainer over which was erected a shower head for spray-washing; a Sturtevant grinder supplemented with screen-bottomed boxes for hand classification; and a thermostatically controlled, electrically heated, forced draft, drying oven (last two not illustrated).

Fig. 3 Reaction Kettle

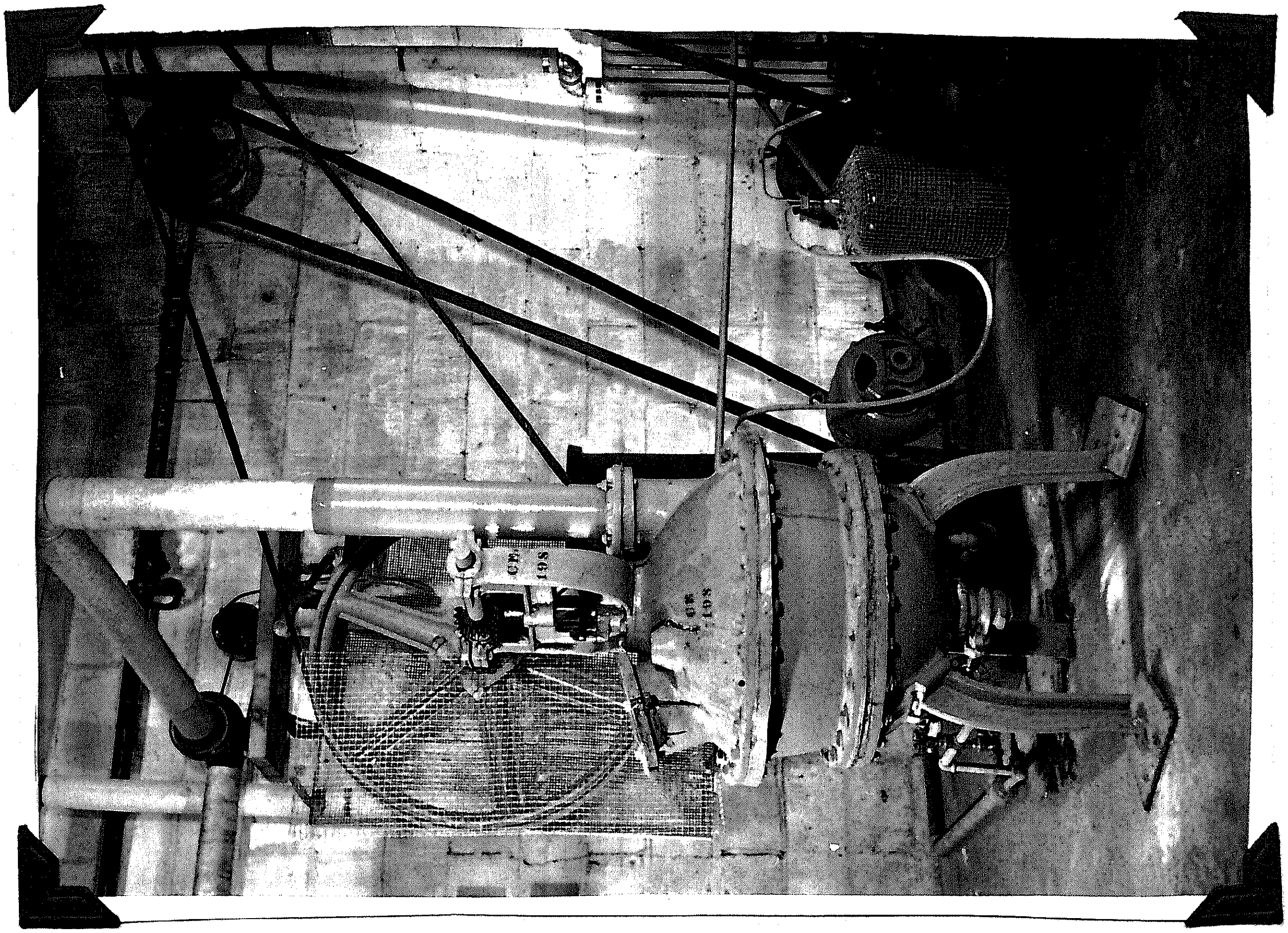


Fig. 4 Opposite side from Fig. 3 showing Filter and Kettle

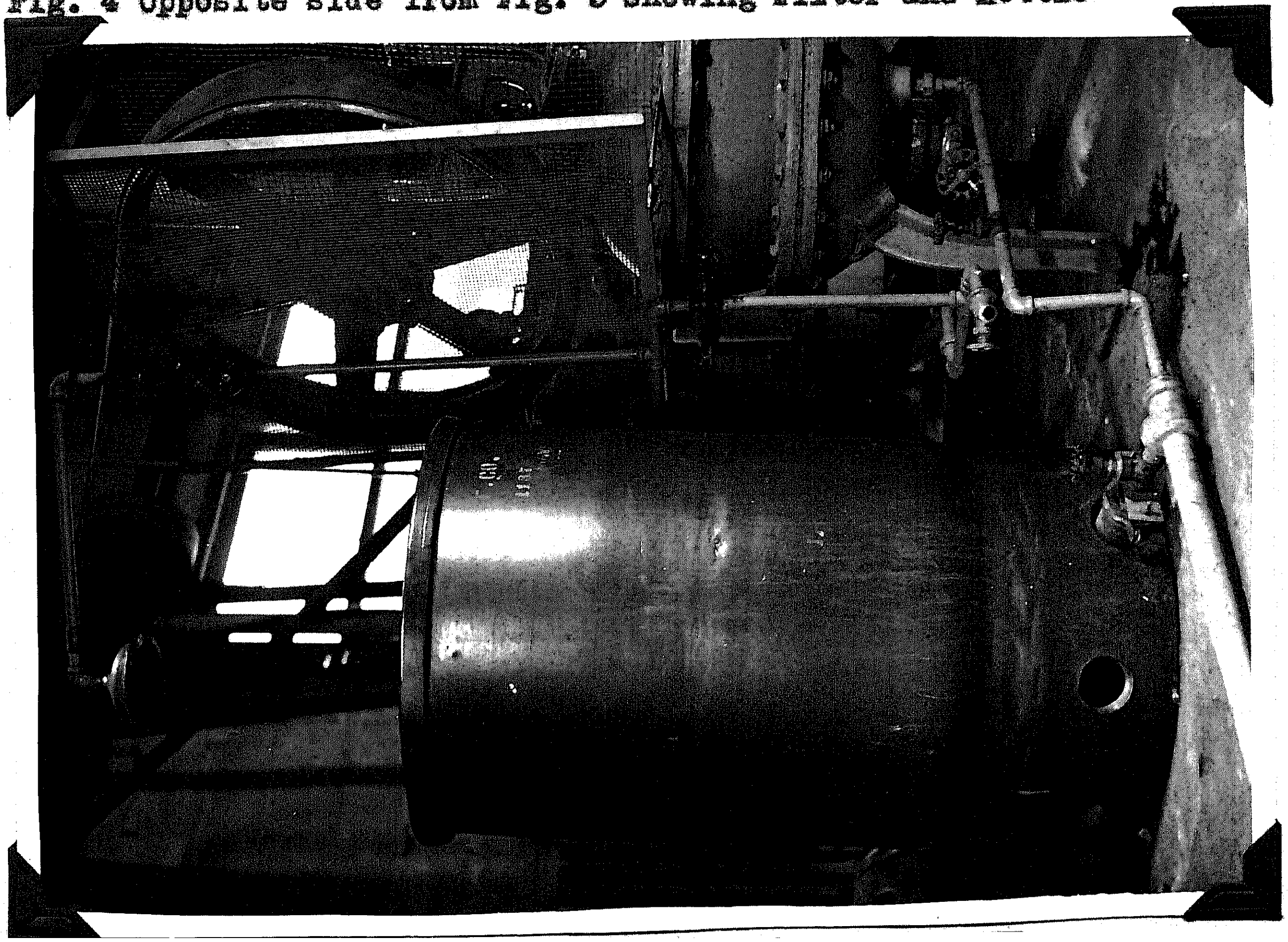
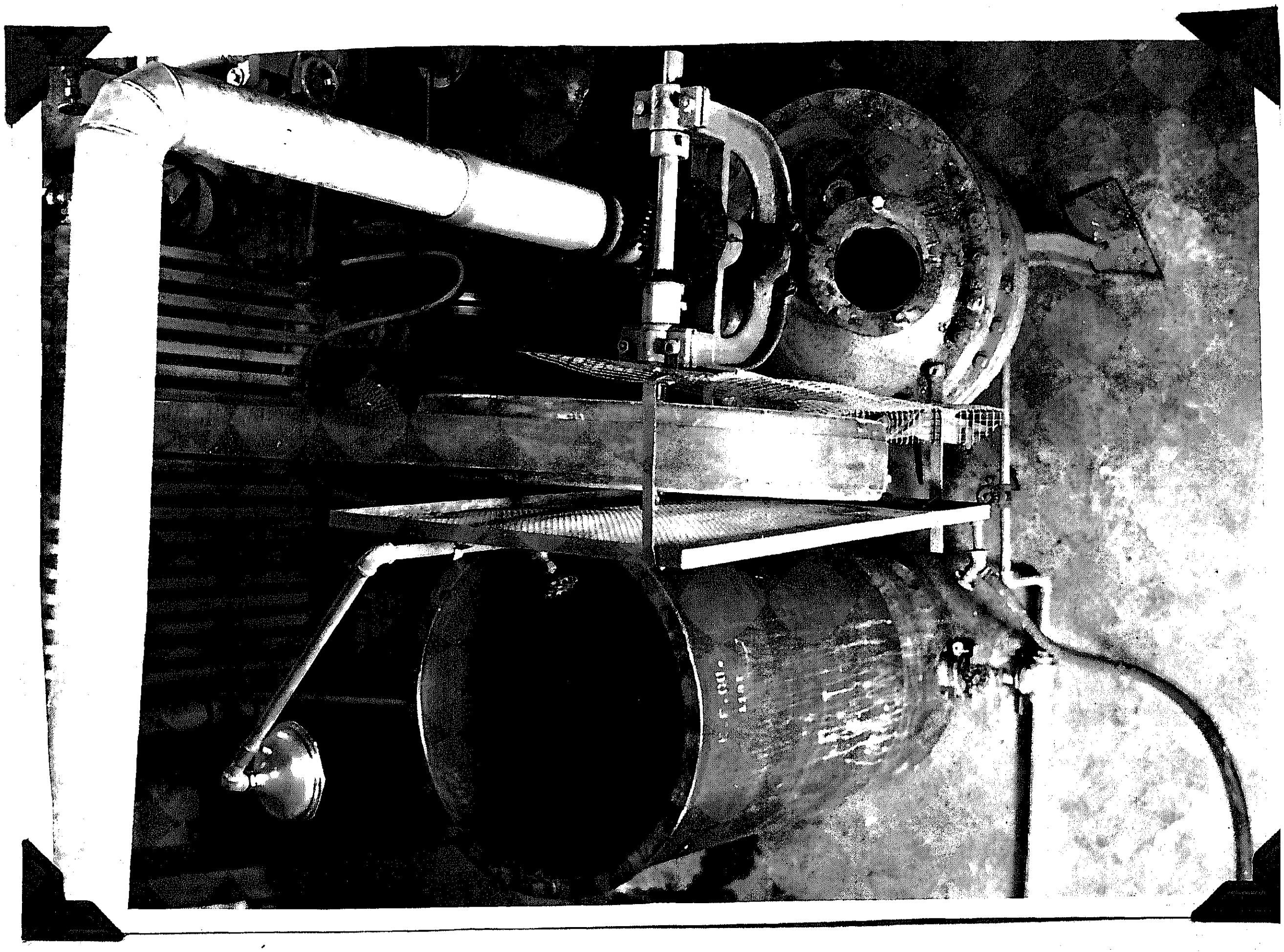


Fig. 5 Top View of Apparatus



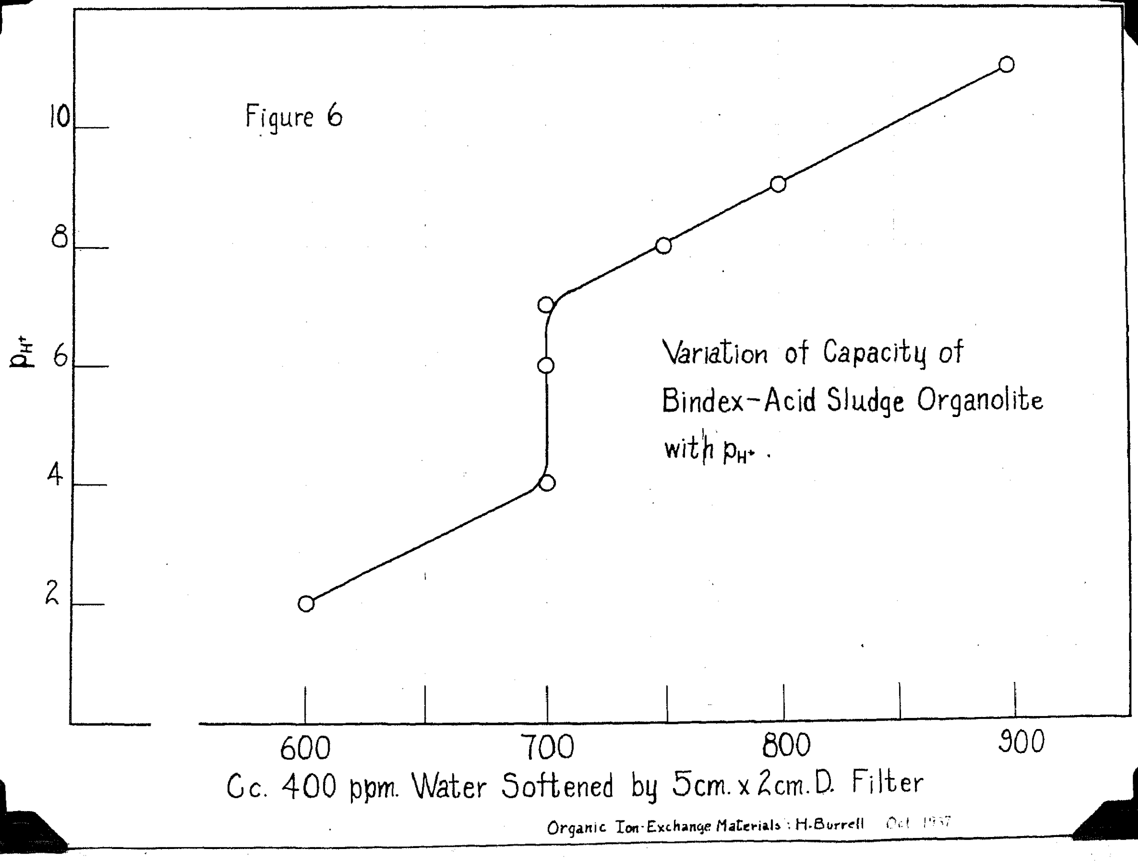


Figure 6

Variation of Capacity of Bindex-Acid Sludge Organolite with p_{H^+}.

Organic Ion-Exchange Materials : H. Burrell Oct. 1937

In the kettle were placed 25 pounds of acid sludge from white oil refining. The blower was turned on and the sulphur dioxide was sucked out of the kettle but the blower leaked around the shaft and the room filled with sulphur dioxide. The stirrer was started and 5 pounds of Bindex (dried hemlock sulphite liquor) were gradually added. This was very powdery and much dust was sucked out of the kettle by the fan. The reaction mixture spontaneously warmed to 40° C. Steam was admitted to the jacket of the kettle, but either because of low boiler capacity or poor heat conductivity the temperature did not rise above 45° C. The mixture became so viscous that the belt continually slipped off the pulley. The belt was tightened and then the bushing gave way so that the pulley turned while the shaft was held stationary. The stirring load was too great.

The batch was allowed to stand in the kettle over night. In the morning it was very hard. The kettle was heated by passing steam through the jacket, and the material could then be peeled off the walls and pulled out through the man hole. The large lumps would not permit washing, so they were coarsely ground with the Sturtevant grinder.

The material was placed on the filter and sprayed with water. The vacuum would not pull the water through because the fines clogged the filter and a jelly-like layer settled on top of the base-exchange material. It was hence washed by decantation and dried. The yield was 4.2 pounds.

IVA2b

Another batch was made in the repaired apparatus as in IVA2a. This time the kettle and the sludge were heated to 45° C. before the Bindex was added. The following heating schedule was then followed:

Minutes Elapsing	Temperature of Mix, ° C.
0	45
2	65
7	70
15	77 (The steam to jacket was shut off at this point.)
25	82
37	82

A stream of water was turned into the kettle so as to soften the mix which was then flushed out of the bottom port, drained, and dried. The yield was 10 lb. of organolite.

Although the experiment proceeded more smoothly than before, it was concluded that the apparatus on hand was not suitable because of insufficient stirring power or the wrong type of stirrer, and also a deficiency of steam heating capacity. The small yield was thought to be caused by insufficient heating. Probably a jacketed mixer similar to a Mastodon (Paul O. Abbe), Imperial Type A (J. H. Day Co.), or a Reado Industrial and Chemical (Read Machine Co.) (27) would prove the correct type of apparatus for the manufacture.

IVB1a

A commercial portable water softener (Permutit Model P-5) was charged with synthetic gel zeolite (Decalso, Permutit Co.), about 3 pounds (1893 cc., measured dry, tamped down in a 500 cc. graduate) being required. A test was made with Montclair, N. J. tap water (which averaged 25 ppm. hardness), but after 1,093 gallons had been softened without exhausting the zeolite, it was decided that the use of the natural water was not feasible, because it was not hard enough.

A 50-gallon tank equipped with a water level gage was set up and the softener was placed at a lower level so that there was a 7 ft. 9 in. drop between the bottom of the tank and the bottom of the softener. This head was of course increased by the height of the water in the tank which amounted to 0.75 inch per gallon.

The tank was filled with tap water and sufficient calcium chloride was added to bring the hardness up to 450 ppm. The water was agitated by blowing air through it for 5 minutes.

The softener was regenerated as follows:

1. The valve was turned to "Wash" and about 2 gallons of tap water were backwashed (i.e., forced from the bottom of the bed up through the top) through the zeolite bed.

2. The valve was turned to "R" (i.e., it was closed), the top of the softener was removed and 500 g. salt added.

3. The valve was turned to "Service" and 1 quart of tap water was run through. (When the valve is turned to "Service," water is allowed to pass downward through the bed.)

4. The valve was turned to "R" and allowed to stand over night.

5. The valve was turned to "Service," and the salt flushed out with tap water.

6. The hard water supply of the tank was connected.

The test runs were made by allowing the hard water to run through at the rate of 12 gallons per hour, each gallon of effluent being sampled for hardness. The pH of the raw water was 7.1; that of the effluent 7.3.

On 5 runs an average of 28 gallons of the 450 ppm. hard water were softened.

IVB1b

The softener was charged with a quebracho-acid sludge product (IVA1b) screened through 14 on 30 mesh.

Using the same conditions as in IVB1a, an average of 10 gallons of 450 ppm. water was softened.

IVB2a

A test for color throwing (i.e., leaching out of brown color from the base-exchange material) was made on several products. A small quantity of the material which had been subjected to several exhaustion and regeneration cycles was placed in a test tube with 10 times its volume of distilled water and allowed to stand for 6 days.

Those found to throw color were: chestnut-sulphuric acid (IB1b), m-phenylenediamine-formaldehyde (IIIA1b), and quebracho-formaldehyde (IA1a). The latter also showed a definite growth of greenish-gray mold, a phenomenon which was also noticed whenever a wet sample of this material was stored.

Among those which did not color the supernatant water in the tube were: quebracho-sulphuric acid (IVA1a), quebracho-acid sludge (IVA1b), peat-acid sludge (IB2d), hemlock sulphite liquor-acid sludge (IB2c), alpha-flock sulphuric acid (IB1f), and redwood-sulphuric acid (IB1f). These tubes were inoculated with the mold which grew on the quebracho-formaldehyde resin, but after 2 weeks there was no growth of mold observed.

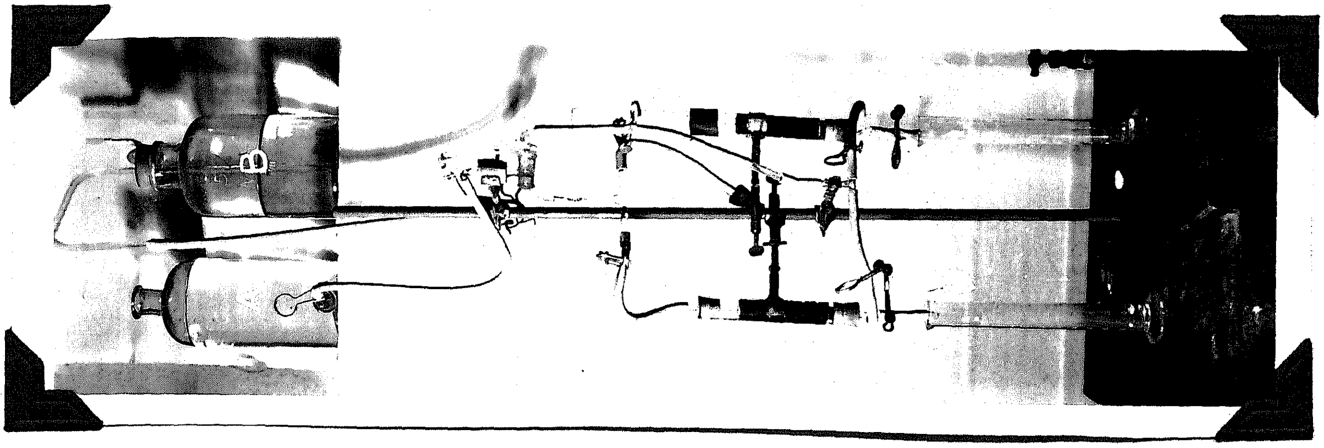
IVB3a

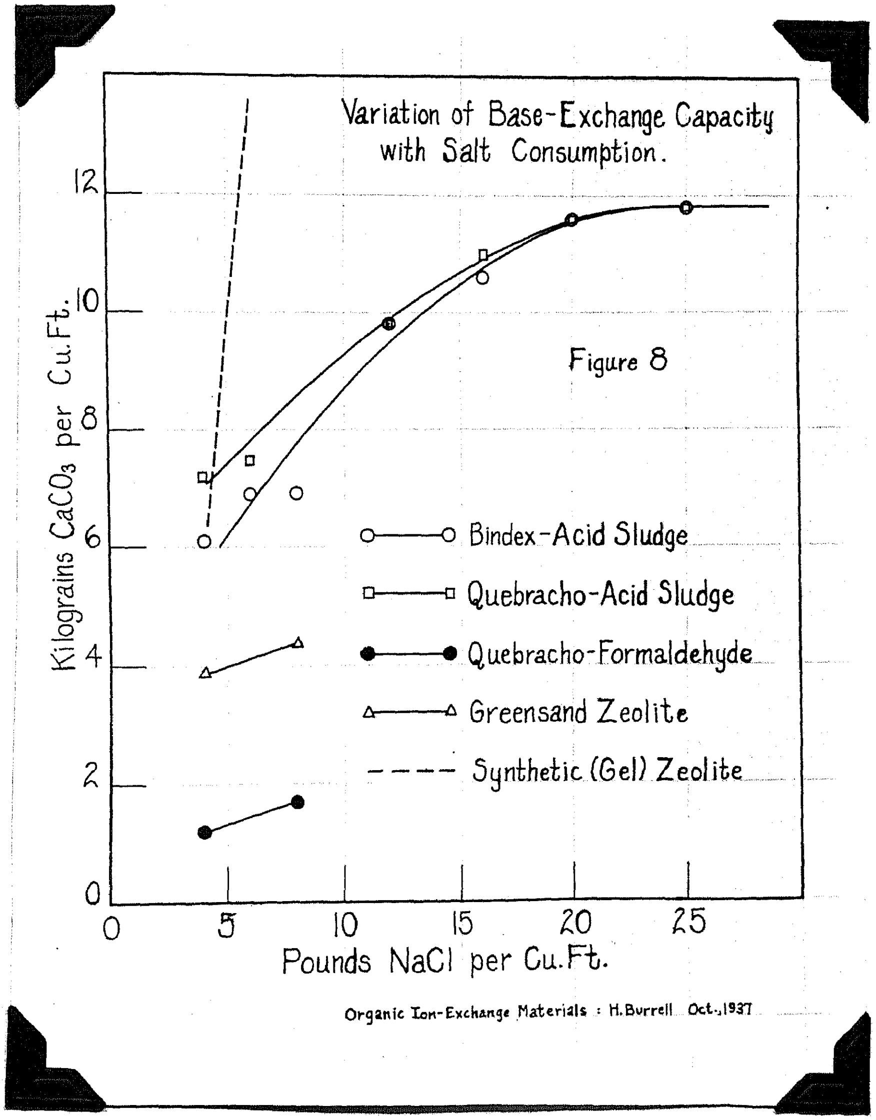
The effect of pH on Bindex-acid sludge organolite (IB2c) was determined on a 2.0 cm. diameter x 5.0 cm. filter column. A 10% solution of sodium chloride was adjusted to pH 2.0 (pH's were determined by La Motte indicators and standards) with dilute hydrochloric acid and used in 200 cc. portions to regenerate the filter which was tested with a calcium chloride solution of 400 ppm. hardness, also adjusted to pH 2.0. This was repeated three times, and the average taken as the exchange capacity at pH 2. The procedure was repeated (adjusting with sodium hydroxide at the higher pH values) at pH 4, 6, 7, 8, 9, and 11. The results are presented graphically in Figure 6 (p. 88) where the volume of 400 ppm. water softened is plotted against the pH. No tendency to dissolve, disintegrate or throw color was noticed.

IVB3b

The method used for determining the sodium chloride consumption or amount of hardness ($CaCO_3$) removed per pound of salt differed slightly from the general method. The apparatus used is shown in Figure 7. Tubes I and II contain 10 cm. x 2 cm.-diameter filter beds of organolite. The material, which was screened through 20 on 40 mesh sieves, is supported on a 2 cm. perforated porcelain plate which is separated from the lower one-hole stopper by glass beads (E). Into this stopper is inserted a T tube which may be used for drainage into cylinders (D and D') or (with proper setting of stopcock C) for directing a stream of wash water upward through the bed. On top of the column

Fig. 7 Sodium Chloride Consumption Apparatus





lies another perforated plate for distributing the water flowing downward through the tube inserted in the upper stopper. Stopcock (C) is used with the various clamps so that hard water (from bottle A) or brine (from bottle B) may be passed either upward or downward through the columns.

At the start of the cycle, the upper stopper and perforated plate were removed and an identical glass tube (F) was connected with the one containing the organolite by a short length of rubber tubing, as shown on tube II. Hard water was introduced at the bottom, washing the organolite granules upward until the suspended volume was about 45 cc. When the granules were thoroughly stirred up, the flow was stopped and they were allowed to settle and the column was then drained. (It was this settled and drained bed which was adjusted to 10 cm. in height.) The tube (F) was removed, the perforated plate and stopper were replaced (as in tube I) and the desired amount of sodium chloride solution (of 10% concentration for more than an 15 lb. of salt per cu. ft., and 5% for less) was run downward through the bed. The stopcock was then set so that the 400 ppm. hard water would percolate downward (at the rate of 300 cc. per hour, controlled by Hoffman Clamps (G) and (G')), and the first 50 cc. were discarded as wash water. Each succeeding 100 cc. portion was titrated for hardness with soap and when an effluent containing 5 ppm. hardness was obtained, the cycle was repeated. From the average of the volumes of water softened on three determinations, the kilograins of calcium carbonate removed for each amount of salt used were determined by the following formula:

$$E = V \cdot \frac{H}{10^6} \cdot \frac{28,320}{B} \cdot \frac{15.43}{1000} = 0.000435 \frac{VH}{B}$$

where

E = Exchange capacity in kilograins calcium carbonate per cu. ft.

V = Volume (cc.) water softened.

H = Hardness of water in ppm. (400)

B = Volume (cc.) of test bed. (31.4)

28,320 = cc. per cu. ft.

15.43 = grains per gram.

With the test bed used, each 10.0 cc. of 5% sodium chloride solution were equivalent to 1 pound of salt per cu. ft.

Determinations were made on quebracho-acid sludge (IB2b), hemlock sulphite liquor (Bindex)-acid sludge (IB2c), quebracho-formaldehyde (IA1a), and greensand (Zeodur) materials. The results are plotted in Figure 8 (p. 97). Since it is not customary to regenerate with more than 10 lb. salt per cu. ft., the left-hand portion of the graph gives an indication of capacities under operating conditions. It may be seen that at 4 and 8 pounds of salt per cu. ft., the acid sludge materials possess a higher capacity than greensand, while that of the quebracho-formaldehyde resin is less than the greensand.

The (broken line) curve for gel zeolite was not determined by this method but was plotted from data in the literature (<u>123</u>) merely for comparative purposes.

Theoretical Considerations

Constitution of Zeolites

The term "zeolite" originally was restricted to a particular class of minerals, but usage has broadened the meaning to include most substances which can be used to soften water by base exchange. (Whether organic, base-exchange materials are to be classed as zeolites will probably be determined by the nomenclature in publications of the next few years; the subject is so new that there is no agreement among authorities as yet. Mr. Carleton Ellis has suggested that this class be called "Organolites." In this thesis, "zeolite" will be restricted to inorganic, and "Organolite" to organic, base-exchange materials.)

The two prevalent types of zeolites are greensand (also called natural, or glauconite) and synthetic (also called gel, or precipitated). The chemical composition of the zeolites varies according to the source and the treatment which has been given them. There is but little correlation between the quality of the greensand type and its chemical make-up; most greensands on the market have essentially similar compositions, but their properties vary rather widely (123). The gel type has been quite thoroughly investigated, and it has been found that there are limits between which the composition should lie. If the composition of the regenerated state is expressed as $(Na_2O)_x \cdot (Al_2O_3)_y \cdot (SiO_2)_z$, then the ratio x:y:z should fall within the range 1:1:4 to 1:1:15. In general, an increase in SiO_2 content decreases the tendency to dissolve in raw waters but also decreases the exchange capacity.

While commercial zeolites are practically limited to combinations of sodium oxide, alumina and silica, several proposals have been made to substitute other constituents for the last two. Boehringer prepared a gel from sodium silicate and borax having the composition $Na_2O \cdot SiO_2 \cdot 2B_2O_3$ which he used to absorb calcium and magnesium ions from water (19). Earlier, he as well as De Brünn (30) produced complex compounds of silica and amphoteric oxides of metals such as tin, zinc, lead, zirconium, and titanium, which they used to soften water. Theriault describes a "biozeolite" (121) present in activated sludge of treated sewage which has the formula $0.84M_2O \cdot R_2O_3 \cdot 3SiO_2$ where M is sodium or equivalent and R is either aluminum or iron. A process for making artificial zeolites in which the silica was replaced by boric, phosphoric, nitric, sulphuric and other inorganic acids and their salts was also patented by Riedel (101).

Besides the above mentioned oxides, zeolites always contain some water. Although the amount is variable it is thought to play an important part in the mechanism of the base exchange (47). The water is held in the same manner as it is in gels and not as in hydrated salts (104).

Theory of Base Exchange

The chemical equation representing the base exchange reaction as applied to water softening is usually set down in some such form as:

$$\mathrm{NaZe} + \left\{\begin{matrix} \mathrm{Ca}^{++} \\ \mathrm{Mg}^{++} \end{matrix}\right. \underset{\text{Regeneration}}{\overset{\text{Operation}}{\rightleftarrows}} \left.\begin{matrix} \mathrm{Ca} \\ \mathrm{Mg} \end{matrix}\right\}\mathrm{Ze} + \mathrm{Na}^{+}$$

where Ze represents the zeolite "radical." This means that the sodium zeolite combines with those elements causing water hardness until equilibrium is reached, when no more of the calcium or magnesium in the raw water will be taken up. The reaction may then be forced to the left by placing the calcium and magnesium zeolite in contact with an excess of sodium ions (i.e., salt brine), whereupon the sodium zeolite is regenerated and it may be again subjected to the reaction to the right. The equation, however, merely begs the question of how zeolites operate, for such a schematic representation does not elucidate in the way a true chemical equation does. The fact of the matter is, there exists no entirely satisfactory theory which will explain the mechanism of base exchange (12).

However, Austerweil has proposed an hypothesis (7) which, although still a matter of controversy, is rational and illuminating. (It should be remembered that the reaction is not confined to sodium and calcium but occurs with any pair of cations.) Base exchange reactions may be scientifically treated with mathematical precision by considering them to be extraction phenomena in which the solid zeolite is an immiscible solvent with the liquid (water) phase. As such, if the conditions be simplified so that only two cations exchange (e.g., potassium and calcium) the extraction law of Bertholet and Jungfleisch pertains. In addition, the laws of mass action and phase rule are superimposed with the result that extraction is accompanied and limited by an equilibrium of the two cations in solution. When a potassium zeolite is added to a solution containing calcium ions, equilibrium is "determined by the quotient of the concentrations (or solubilities) of the two zeolites present, the original one and the newly formed, in the aqueous solution, the latter one being constantly produced until the limit of its solubility is reached, these two being the two least soluble components of the system."

The equilibrium may be expressed by using an "exchange coefficient," a (analogous to Bertholet's repartition coefficient); a is, then, a number less than unity which is the mol fraction of zeolite-cation which will have exchanged with a corresponding amount of solution-cation when equilibrium is reached; it is solely dependent on the concentration or solubilities of the two least soluble phases, in conformity with the phase rule. "The total extraction of a cation in solution with a base exchanger will be possible only with an infinite amount of zeolite (60)." But by setting E equal to a limited but fairly complete degree of extraction (say 99%), the Bertholet and Jungfleisch law may be modified to

$$n = \frac{\log (1-E)}{\log (1-a)}$$

The formula is identical with the extraction equation, being only an expression of a special case where n represents the units of a non-miscible solvent extracting repeatedly an amount of solution equal to 1 unit of solvent.

The limit of base exchange of any pair of cations is limited by the equation,

$$\frac{a}{(1 - a)} = (f) \frac{S_z}{S_{z'}}$$

where S_z and $S_{z'}$ are the solubilities of the two zeolites.

Doubtlessly, the lack of a comprehensive theory is due to the number of factors which influence the reaction so that no theoretical law (including the above) holds in practical applications. Among these may be mentioned (1) heterogeneity of zeolites; (2) ratio of alumina to silica (which effects the solubility of the zeolites); (3) side reactions (aluminum is partially replaced, as well as the sodium, by iron, chromium, manganese, etc.); (4) basic zeolites precipitate heavy metals as oxides or hydroxides which are themselves weak bases; (5) pH; (6) several cations rather than just two are usually present; (7) the accompanying anions; (8) rate of flow (about 30 minutes are necessary for equilibrium); and (9) viscosity (sugar solutions do not exchange to the same extent as less viscous ones. This seems to show that the reactions are not only carried out at the surface of the mass, but also at least partly at the surface of the capillary channels). By carefully choosing conditions, however, Austerweil substantiates his theory from experimental data.

In Germany, explanations have followed the laws of ionic reaction with some success. Jenny (60) has discussed and reviewed this angle comprehensively. He has advanced a modified Helmholtz double-layer concept, i.e., the micelles consist of an "ultramicron" — an inner layer of anions and an outer layer of cations. Displacement depends on attraction of inner and outer layers as well as hydration (133).

The colloidal concept is given by Turner and Jackson (125) who argue in part, "The manufacture of artificial zeolites demonstrates unquestionably their highly complex colloidal gelatinous nature, for they are prepared by complete gelation and .... must therefore be highly absorbent," and conclude, "In the light of present evidence it would appear that the zeolite process involves ionic reactions and that these reactions are profoundly influenced by the degree of hydrolysis or hydration of the salts and ions concerned. The actual forces involved in promoting the reactions, however, include adsorption and other surface and structural phenomena, familiar in the field of colloid chemistry."

In investigating the structure of zeolites by x-ray photographic methods, Pauling (89) conceived a structural unit, $8Na_2Al_2Si_3O_{11} \cdot 2H_2O$, face centered and with a structure such that water can escape, on heating, through channels along the axis (001). In base exchange operations, sodium ions can escape along the same channels. It has also been postulated (129) that the silica serves only as a suitable physical medium without playing any direct part in the exchange process.

Factors Affecting Practical Applications

In spite of the widespread use of zeolites in water softening, no adequate text has appeared to instruct operators or investigators in the difficulties and complications of the process. One must depend on possibly prejudiced manufacturers' bulletins or go back to the original literature which still contains inconsistencies and diversity of opinion. Further, it is evident that the great number of factors which must be considered in practical applications is discouraging to the accurate analysis of any problem. Nevertheless, certain principles have been more or less empirically derived, and their applications are clear in a qualitative way, but the value to be ascribed to each must be assigned almost entirely on the basis of experience. Some of these will now be briefly discussed.

(1) The Base-Exchange Capacity is, of course, of paramount importance. It is conveniently and satisfactorily stated as the weight of hardness (as calcium carbonate) removed per unit volume of zeolite (e.g., grains per cubic foot).

(2) Much confusion and disagreement has resulted as to the exchange capacities and methods of determining them because of the variables inherent in such determinations. The Ultimate Exchange Value (123) is the total capacity of a given material. It is the differential between complete exhaustion and complete regeneration; but these two conditions are never realized commercially because to obtain the former, concentrated solutions of calcium and magnesium salts

are necessary to exhaust all the sodium base in the zeolite; and to obtain the latter such a great excess of salt is required as to make it uneconomical. Consequently, the Ultimate Exchange Value is never utilized in practice. It is of value in theoretical and comparative considerations, however.

(3) The capacity range actually used in practice may be termed the Operating Exchange Value. This is not a constant figure even for the same zeolite, but varies with different installations according to hardness of raw water, cost and quality of salt and other interdependent factors. Naturally, the numerical value is kept as close to the Ultimate Exchange Value as is economically possible. It is the value which laboratory tests on commercial materials usually strive to approximate. Much useful data has been reported, however, which falls between these two conceptions; as long as conditions under which tests were made are reported, a reasonable interpretation of results may be made.

(4) The amount of sodium chloride required per unit of hardness removed is very important. The cost of

salt is probably the largest single item in the operating expense. Obviously, a zeolite may have a high Ultimate Exchange Value but require so much salt to attain it, that its operating cost may be prohibitive. On the other hand, several zeolite plants use sea water or brine wells for regenerating with the resultant nominal salt cost. The ratio of salt required to hardness removed is probably more fundamental than any other single factor. Typical values are 2700-3800 grains calcium carbonate per cu. ft. using 1.4 lb. salt per cu. ft. for greensand zeolite, and 6000-20,000 grains per cu. ft. using 4 to 8 lb. salt per cu. ft. for synthetic (gel) zeolite. Here again, these values are only relative and depend on pH, hardness of water to be treated, etc.

(5) In connection with salt requirements, a condition of operation to be avoided is under-regeneration. If too little salt is used (e.g., inadvertently or in a mistaken attempt to practice economy) in the regeneration cycles, the capacity of the zeolite may be permanently lowered.

(6) A similar danger is overrunning. If the operation of the softener is continued after it has ceased to deliver soft water, the capacity on subsequent cycles is also lowered. It may usually be brought back to normal, by carefully operating a few cycles, possibly overregenerating somewhat.

(7) The wash water requirement is an item of considerable expense. This water is that which is required immediately after the regeneration step in order to wash out excess brine and also those ions causing hardness which are now in solution by virtue of the base exchange reaction with the regenerant. Such water is, of course, run to the sewer and must be considered an item of expense. Walker and Collins (130) report in the installation at the Beacon Street Plant of the Detroit Edison Co. that the wash water represented 10.2% of the operating costs. Behrman (12) estimates the normal wash water requirements of a synthetic zeolite to be 5 to 10 per cent of the total volume of water softened, and that of glauconite to be 20-25%. Since the absolute volume of wash water

required varies with the size of the bed, the per cent of the total volume treated varies inversely with the exchange capacity.

(8) The rate of flow of water being softened and rate of regeneration vary with materials and results desired. If an incompletely softened water is satisfactory (as it is in many cases) the water may be forced through at a high rate with the result that a large volume of water is partially softened. The capacity also varies with rates of flow lower than the maximum at which completely softened water is obtained. The time required for regeneration is less than one-half hour for greensand and slightly greater for synthetic zeolite, but the old fused synthetic type required 8 to 12 hours.

(9) An important quality of zeolites is the resistance to abrasion. The friction of the water on the granules and the granules on each other wears them down so that there is loss of material as well as contamination of water. Toughness and hardness are therefore desirable in the material.

(10) Physical strength, i.e., resistance to crushing, is a related characteristic.

(11) The density or weight per cu. ft. is a factor having several ramifications. The water content of gel zeolite varies widely for it is necessary to ship it fairly moist to improve physical strength. Hence density should be considered on a bone-dry basis in comparing amounts of two zeolites. But since equipment is designed with volume as a primary consideration, the weight per unit volume as used (wet) is also necessary, and this varies slightly with the method of measurement as the granules may pack loosely or tightly under varying conditions. The grain size, of course, also affects the density. Other things being equal, a heavy zeolite is better because it indicates more compact and stronger granules and is less liable to be carried away in the backwash. On the other hand, when zeolites are sold on a weight basis, a low density is beneficial because less is needed to fill a softener.

(12) Porosity must also be taken into consideration, for besides affecting density, a more porous material

is liable to become clogged by turbidity or iron in raw water (although this has been denied by a few investigators (7)). Conversely, a more porous material affords a greater surface so that the capacity may be higher.

(13) The grain size must be balanced between the fact that the capacity varies inversely with the mesh of the material (18) and that extremely fine grains may be washed away, and they pack together, thus greatly increasing head loss through the filter (54, p. 52).

(14) The resistance to aggressive attack is often the deciding factor in determining the choice of zeolites for a given water. This is equivalent to the rate of solution. An immoderately low or high pH, a low silica content, or a high carbon dioxide content in the raw water all tend to dissolve the zeolites. This not only causes loss of material, but contaminates the effluent and clogs the filter. Although synthetic zeolites are particularly sensitive to such aggressive waters, organolites are exceptionally inert.

(15) The silica content of the raw water not only effects the deterioration of the zeolite, but the

effluent of zeolite-softened waters always contains some silica, a fact which is of great importance in view of the findings of the Bureau of Mines (98) that the presence of silica is necessary for development of caustic embrittlement in boilers. Organolites do not so contaminate the softened waters.

(16) The pH of the water and regenerating solution must not be overlooked, for aside from attack on zeolites, the effluent may be useless unless this factor is controlled.

(17) The hardness of the raw water influences the capacity of the zeolite. It does not alter the rate of passage of raw water but changes the time allowable between regenerations.

A greater amount of calcium and magnesium may be removed from softer (less concentrated) water, a greater volume, of course, being treated. The relative proportions of calcium and magnesium ions also effect the exchange capacity, for it varies somewhat for the two (78 and 54, p. 52). It is not desirable to use a water with hardness less than about 150 ppm. with gel zeolites (123).

(18) The anions present in the hard water increase to some extent the capacity of zeolites, according to the lyotropic anion series (126) (CNS, I, CrO_4, Br, Cl, NO_3, SO_4, ClO_3 (73)).

(19) Cations other than calcium and magnesium comprise another factor to be considered. Iron and manganese are commonly present; ferrous iron is absorbed and regenerated along with the hardness, but ferric iron tends to coat the granules and clog the pores. Manganese cannot be removed by regenerating with brine, and so in normal operation it lowers the efficiency. (It may be removed by regenerating with potassium permanganate, however.) In general, it is better for both iron and manganese to be absent (2, 54, 65). Aluminum ions are deposited in the zeolite, destroying the correct chemical composition and decreasing the efficiency (1). Other ions such as lead, copper, and tin are absorbed and removed by regeneration with brine (except lead which requires such a salt as sodium nitrate) (103).

(20) Other impurities should also be reckoned with. Turbid or muddy water coats the granules and clogs

the pores and so lowers efficiency. Oil and hydrogen sulphide cause similar impairment (54, p. 52-3).

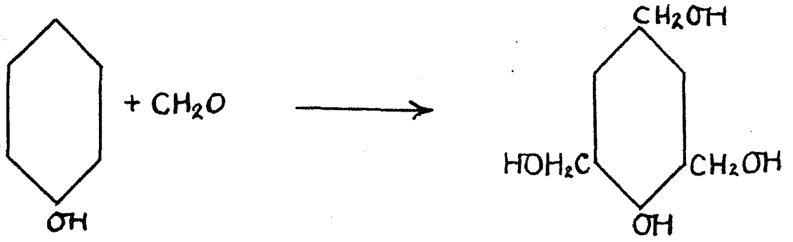
This maze of interdependent variables, while pertaining especially to zeolites, are also largely applicable to organolites.

Constitution of Synthetic Resins

Adams and Holmes (3) open their paper with the assumption, "In virtue of the possible possession of acidic properties by phenolic resins, and their stability under a variety of conditions, it was thought that they might form insoluble salts with bases," which probably is the correct explanation of the base-exchanging properties.

When a monohydric phenol is condensed with formaldehyde to yield a resin, the exact details of the chemical processes taking place are still a matter of some controversy. In a somewhat simplified form, the mechanism is as follows:

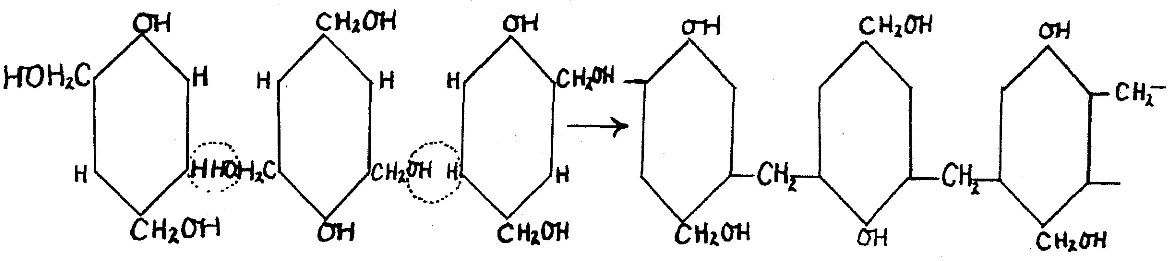
phenol plus formaldehyde yields o- and p-phenol-alcohols,



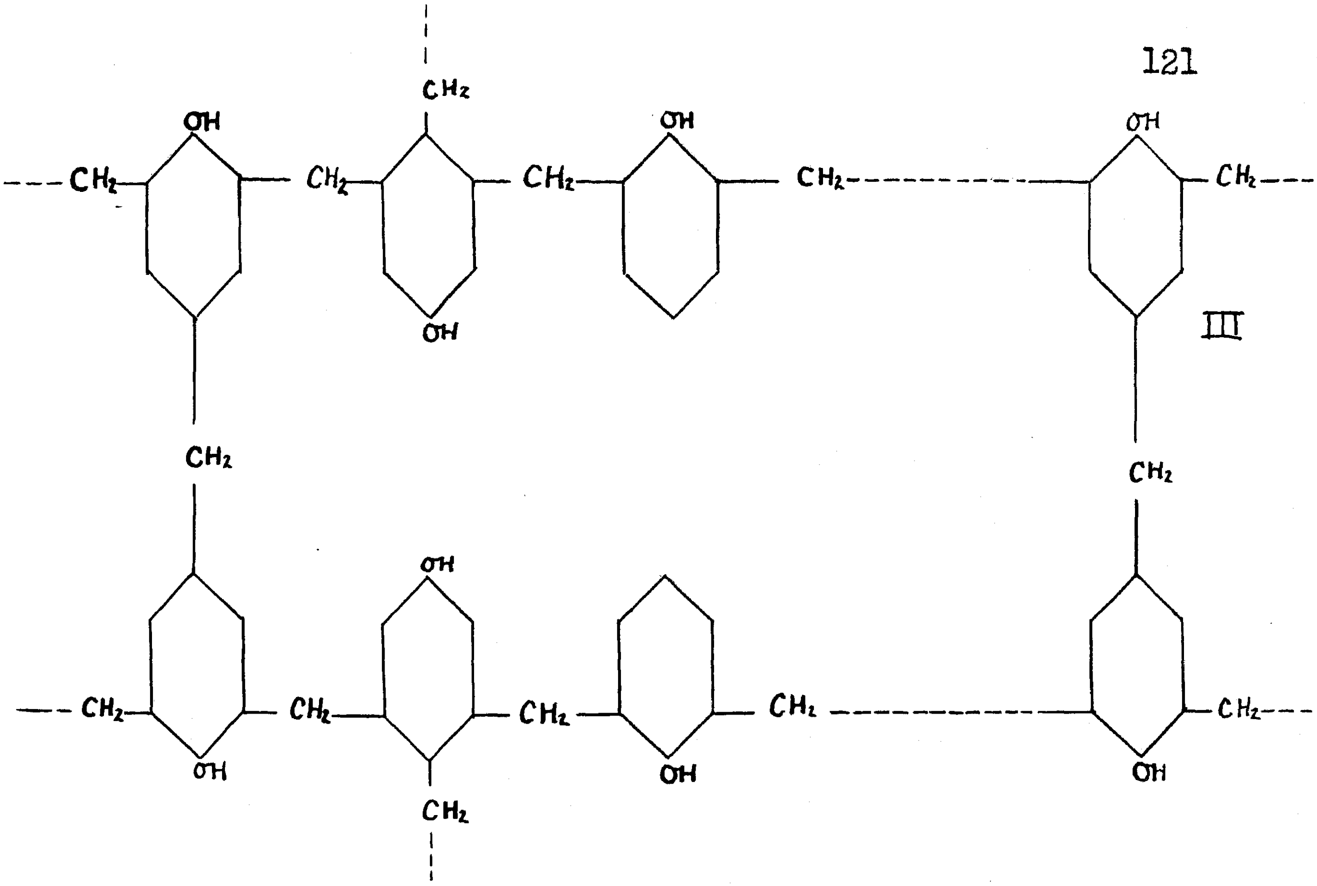
I

which condense with elimination of water to form linear polymers,

II



which are easily thrown over to three-dimensional polymers by a few cross linkages (34, 35, Chapter 14).



III

As a substance polymerizes, that is, as its molecular weight increases, its physical properties vary in a regular fashion, regardless of what the substance is. Thus, its boiling point and melting point are raised, it becomes more insoluble in water, etc. (35, Chapter 4; 107). It is therefore desirable to attain molecules as large as possible when condensing phenols with aldehydes for water purification, because insolubility in water is a primary requisite.

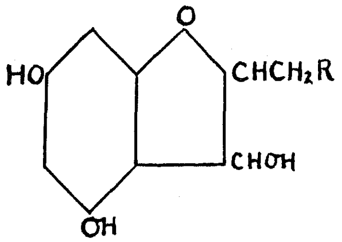
It may be expected that a trihydric phenol such as pyrogallol or phloroglucinol, or a dihydric phenol such as resorcinol or catechol will react more rapidly with formaldehyde and to a more highly polymerized state than a monohydric phenol. It is well known that resorcinol reacts almost instantaneously (note also Experiment IA3a), and the extremely rapid gelation of quebracho is shown in IA1a. In contrast, phenol or cresol usually require a longer time before the gelatinous stage is reached (46). The reason for this is apparent when we examine the structural formulas of the polyhydric phenols and see that the number of reactive atoms on the benzene ring is increased by virtue of there being more ortho and para positions than in a monohydric phenol, and further, that some are doubly reactive because they are simultaneously ortho and para to different hydroxyls (cf. Equation I above). Consequently, as may be expected, formaldehyde reaction products become extremely insoluble since they are very large molecules studded with phenolic groups which are probably functional in base exchange as postulated by Muller (77).

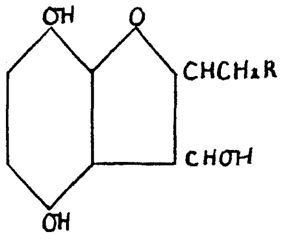
Evidence supporting this hypothesis is presented in IA2c, where it is shown that a logwood extract (hematoxylin — probably 3,4,3',4'-tetrahydroxyrufenol) resin is active whereas that from the oxidized extract (i.e., phenolic groups presumably have been converted to quinoid structure) is inactive. (Cf. also IB1a with IB3d, and IB1b with IB3e, where oxidizing acids have been used.)

Since tannins are high molecular weight derivatives of polyhydric phenols of the catechol or pyrogallol types (<u>29</u>, <u>120</u>), their action is similar to the phenols themselves.

Variables Investigated

The reason for wide variations in capacities with different resins is not clear. As mentioned by Adams and Holmes and substantiated in IA2a, monohydric phenolic resins possess no water-softening properties. Referring to the table reproduced here as Table II (p. 254), it may be seen that phloroglucinol resin absorbed the calcium from 400 cc. of solution, whereas pyrocatechol, catechin, resorcinol, and quinol resins absorbed none. Further, quebracho tannin, for which the following formulas have lately been proposed (82), produced a material which softened 600 cc.





$R = 3,4(OH)_2C_6H_3$

If we compile the tannins known to produce active products, we see that quebracho (IA1a), fustic (IA2d), logwood (IA2c), larch, wattle, acacia, gambier, and cutch (last five from Adams and Holmes, although IA2d does not agree regarding gambier and cutch) are all of the catechol type; whereas those which are inactive, viz., gallic acid (IA2b), tannic acid (IA2b), chestnut (IA2d), and sumac (IA2e) are all of the pyrogallol type (75, 97, 120). While the evidence is not conclusive, it appears that only the catechol type can soften water. It should be noted (even though the connection is not now clear) that catechol tannins have no combined glucose, whereas pyrogallol tannins have.

The variables discussed on pages 109-119 apply to synthetic resins for the most part. Certain diffences to be noted are: lower exchange capacity than zeolites, somewhat less physical strength and resistance to abrasion, high resistance to aggressive attack, absence of silica in water, tolerance of wide pH variation, and selective absorption with various cations.

In connection with the formation of the resin itself, it is shown in IA3a, -b and -c that besides formaldehyde, acetaldehyde and acetone may be applicable, but suitable resins are evidently not to be had by using higher aldehydes. Also, reaction in the cold inhibits development of proper physical qualities (IA1c — see IIA3a, substance 6, however).

The fact that phenolics are definitely active instigated the examination of other classes of resins in experiment series IC in spite of the blanket conclusion of Adams and Holmes that "only the polyhydric phenol resins possessed appreciable adsorptive properties." It was thought that it might be possible to prepare an amphoteric resin which would absorb both anions and cations by reacting a polyhydroxyamine with a polybasic acid according to the usual alkyd resin synthesis (35, Chapt. 42-49). For instance, polyesters may be formed from triethanolamine and phthalic anhydride which theoretically might retain anions by virtue of the amino groups and cations by free carboxyl groups. This was done in IC1a; some trouble was experienced in obtaining a sufficient degree of insolubility, for alkyds are rather easily swelled and hydrolized by water. Since the base exchange reaction is largely a surface one, inert granules (sand) were coated with the resin (IC1b). This allowed passage of water, but no absorption of calcium or of chloride ions was detected. Apparently the polyesters are too sensitive to water to be of value in this instance. Similar attempts to prepare amphoteric materials from aminophenols (IIIA2a and b), mixed phenol- and aniline-formaldehyde (IIID1a), and bone oil (IIID2a) were to no avail.

Urea resin was likewise inactive for water softening (IC2a and -b). It did extract gold from dilute solution, however (IIA2a, substance 2); this was probably caused by reducing action of the formaldehyde present, since the white resin became purple colored (colloidal gold) after the auric ions were sorbed.

Natural resins, unmodified and reacted with various reagents, were also ineffective in calcium absorption (IC3a, -b, and -c).

Constitution of Acid Resinoids

The reason for base exchange in those organolites prepared by treatment of various materials with strong, concentrated acids is not as clear as in the case of the synthetic resins. The structures of the compounds are unknown. Indeed, it is not likely that any definite compound is produced in any specific case.

When a vegetable product such as a tannin is mixed with concentrated sulphuric acid (as in IB1a or -b) a number of reactions occur simultaneously. Sulphonation, sulphation, oxidation, dehydration, and polymerization probably all play a part in rendering the products insoluble. Here again, as with the synthetic resins, certain functional groups such as phenolic and perhaps sulphonic are the active principles and are held water-insoluble by the large molecular residue which in this case is highly carbonaceous. Evidence favoring the theory of functional phenolic groups is presented by a comparison of IB1a with IB3d and IB1b with IB3e. Here we see that substitution of sulphuric for a more oxidizing acid, which presumably would convert phenolic hydroxyls to quinoid groupings, destroys the activity. The use of an already oxidized vegetable component is also unavailing (note hematine in IB1d). That sulphonic radicals may also be active may partly explain why substitution for sulphuric by other strong acids reduces or extirpates activity as in IB3h (cf. IB1c), IB3a and -b (cf. IB1a and IB1f), IB3c (cf. IB1f), and IB3f and -g (cf. IB1c).

It is rather anomalous that sulphonation should produce insolubility since the process is frequently used to obtain the opposite effect. This suggests that the acid might be operative because of its carbonizing properties. But this is not true _per se_. In IB1f it is shown that simple carbonization (by heat) is not effective, whereas acid treatment is; further, active carbon will not base exchange (IB1h). In addition, certain (unidentified) constituents must be present in the vegetable components. Sugar (IB1h), alpha-flock (IB1f), bran, peanut shells, anthracite, and oak leaves (IBlg) have negligible capacities, although highly carbonaceous products resulted. Substances such as chestnut sawdust or ground bark (IBlg), pine saw dust (IBlf), hemlock needles (IBlg), and redwood flour (IBlf) which consist of a large amount of cellulose and a smaller amount of extractive or resinous substance are more active than straight cellulose (alpha-flock in IBlf) but not as efficient as the extracts themselves (IBla, -b, and -c). Furthermore, the products may be rendered too carbonaceous by over-reacting, as by excessive heat or time, and optimum conditions are usually extant (see IBla, IBlb and IB2b). Although the reaction apparently does not follow the Law of Definite Proportions, a ratio of acid to vegetable component which is most economically desirable pertains (IBlc).

The classes of botanical extracts which are applicable in this process are varied. Catechol and pyrogallol tannins both work (IBla and -b) as contrasted with the situation existing in the formaldehyde condensation products discussed on page 124; and pseudo-tannins such as the sulphite liquors may also be utilized (IB1e and IB2c). Indeed, apparently any extractable substance yields a material with some measure of base-exchange power, although this field has, of course, not been thoroughly canvassed. (Note, however, IB1d, where hematine could not be employed.)

Besides the substitutes for sulphuric acid mentioned in a preceding paragraph, successful results were obtained with a waste product of the petroleum industry — acid sludge. In the manufacture of white oils, for instance, where a specially purified product is required, the petroleum fraction is treated with concentrated sulphuric acid (36) which retains impurities, and, as a bottom layer, is drawn off leaving a water-white oil. The sludge is usually an extremely viscous, tarry, black material with a specific gravity of about 1.4 and an acid content approximating 50% calculated as H_2SO_4. It contains free sulphuric acid, sulphurous acid, sulphonic acids of various types, and hydrocarbon material. It was found that this could be used in lieu of sulphuric acid with almost identical base-exchange capacities being attained in addition to much increased yields (cf. IB2b and IB1a, IVA1a and -b, and note all IB2 series). The acid sludge is, besides, to be preferred because it is cheaper than sulphuric acid. The reactions ensuing with the sludge closely parallel those with sulphuric acid, but it is not a case of mere substitution. The increased yields noted are probably attributable to the combination of the high molecular weight sulphonic acids of the sludge with the tannins, which, of course, affords a resultant higher molecular weight and more insoluble product. The supposition that the tannins or the acid sludge themselves become insoluble by heating, thereby increasing the yield, is ruled out by IB2e, where it is demonstrated that heating does not change the solubility.

The factors pertaining to base exchange in general which have been discussed in connection with zeolites and synthetic resins are also applicable to the acid resinoids. A more detailed comparison of the last two (organolites) will be presented in the following section.

Investigation of Possible Commercial Uses

Water Softening

The effects of hard water have been described by Thompson (122) and may be briefly summarized as follows:

(1) Soap is wasted.

(2) Insoluble soaps cause stains.

(3) Life of clothes is decreased 20 to 50 per cent.

(4) Scale in boiler tubes wastes fuel and causes tubes and sheets to overheat with possible resultant leaks and blowouts. Magnesium chloride hardness hydrolizes in the boiler to hydrochloric acid which corrodes and pits the boiler steel.

(5) Dyes are wasted in textile industries; the scouring of fibers is complicated.

(6) Tannin and other chemicals are wasted in the tanning industry.

(7) Canned vegetables are toughened, the liquid is clouded, and a surface scum is formed.

(8) The use of sizes in paper manufacture is increased.

(9) Dirty cores are formed in artificial ice cakes.

(10) Deposits are formed in domestic hot water systems.

The maximum allowable limits of hardness vary with use from 20-30 ppm. for laundry and similar processes to 50-70 ppm. for canning and about 1500 ppm. for household cooking.

A complete discussion contrasting the base-exchange method with other processes of softening water is beyond the scope of this paper; the desirability of zeolites will be taken for granted. However, a brief summary of advantages and disadvantages of base exchange softening is given because it is helpful in estimating the relative importance of the organolites. Since the lime-soda process is most widely used and is typical of all methods in which chemicals are added to the water used, the presentation will be further limited to a direct comparison of the zeolite and lime-soda processes. A bibliography for the reader interested in a more detailed analysis comprises the references (8, 11, 12, 14, 22, 37, 43, 54, 102, 112,

122) from which the following has been selected:

Advantages of Zeolites over Lime-soda

1. Service is continuous and under pressure; lime-soda requires water storage.

2. Produces "zero hardness"; easy control of exact hardness.

3. Hardness fluctuations automatically compensated for.

4. Softens all types of hardness.

5. No sludge.

6. Simplicity of plant; small floor space; few moving parts.

7. Alkaline effluent beneficial in some cases.

8. Only one chemical needed (NaCl); sea water can be used.

9. Process effected without change of water temperature.

10. Small installations economical.

Disadvantages of Zeolites as Compared with Lime-soda

1. Zero hardness not necessary for many uses, since 15-25 ppm. does not precipitate soap.

2. Alkaline bicarbonate water produced may cause foaming, priming, and embrittlement in boilers, and is objectionable for drinking, cooking, and fermenting.

3. Zeolite disintegrates and gradually dissolves.

4. Acids act on zeolites; iron, etc., deposit on granules and lessen efficiency.

5. Oil, mud, and colloidal matter must be removed.

6. Size of plant depends on hardness of water (not as with lime-soda); very hard water more difficult to soften.

7. Nothing prevents hardened water from passing through when bed is exhausted.

8. Lime-soda removes bacteria and fluorides.

9. Lime-soda allows better pH control.

Thus we see that each process has its respective advantages and limitations. A rough, general rule has been given by Ellms (37) who states that the zeolite process is ideal for waters up to 200 ppm. hardness which contain little bicarbonate; for harder waters or one bearing turbidity of a large amount of temporary hardness, the lime-soda process is much superior. Behrman (12) has estimated that for bicarbonate hardness the cost of lime is about one-half that of salt for softening by the respective processes; and for non-carbonate hardness, the sodium carbonate costs about 25% more than salt.

At this point we may note that the organolites possess all the advantages of zeolites and are happily exempt from many of the disadvantages; this will subsequently be discussed in more detail.

Comparison of the Organolites

It is first necessary to compare the two classes of organolites, so that we may select those which will show up to the best advantage in comparison with zeolites. On the basis of Ultimate Exchange Capacities, which values are approximated by the procedure described on pages 35-39, it is evident from Experiment Series IA that the quebracho-formaldehyde product is the best, and, incidentally, about the cheapest, of the resins. In comparing the capacity found in IA1a with that reported by Adams and Holmes (3), several factors must be considered. First, it should be noted that they record results in terms of weight of resin used (10 g.), rather than in terms of volume, which is preferable (123). If the data is taken from their Table II (abridged form included on page 26 of this report), we may convert capacities to terms of volume as the densities are given. Second, the resin used by them was pulverized to pass through 40 on 100 mesh, which is much too fine for commercial use (greensand zeolite is 20/60 mesh and gel zeolite is 10/40). It has been demonstrated that exchange capacities vary inversely with average particle size (18) so an approximate correction factor may be applied: to convert 40 mesh (0.42 mm. opening) material to 20 mesh (0.84 mm. opening), which was used in the present investigation, we may multiply the capacity at 40 mesh by $\frac{0.42}{0.84} = 0.5$. In the third place, they do not record the amount of brine used for regeneration. It may be taken for granted that a great excess was used, as was done in the writer's experiments. Fourth, the hardness of the Thames water used was 200 ppm. as compared with 400 ppm. used in IAla.

If the data of resins 4 and 6 of Table III (p. 26) are averaged, Adams and Holmes obtain a capacity of 1100 cc. of water of 200 ppm. hardness being softened by 12.5 cc. of resin. Converting this to 31.4 cc. (the volume of resin used in IAla) of 20 mesh material, we have 1100 x 31.4/12.5 x 0.5 = 1400 cc. of 200 ppm. water which is equivalent to the 700 cc. of 400 ppm. water determined in IAla. A good check is therefore obtained.

A consideration of the acid resinoids (Experiments IB) shows a wider choice of products. Those with the highest ultimate capacities (converted to cc. of 400 ppm. water) are collected in the following table:

Table XI.

Product	Experiment	Vol. (cc.) 400 ppm. Water Softened
1. Quebracho-Sulphuric acid	IB1a	1650
2. Quebracho-Acid sludge	IB2b	1650
3. Bindex-Acid sludge	IB2c	1500
4. Bindex-Sulphuric acid	IB2c	1300
5. Chestnut-Sulphuric acid	IB1c	900
6. Chestnut-Acid sludge	IB2a	900
7. Sulphite liquor-Sulphuric acid	IB1e	1000
8. Redwood-Sulphuric acid	IB1f	1000
9. Peat-Sulphuric acid	IB1g	900

A recapitulation indicates the acid resinoids are far superior to the quebracho-formaldehyde resin on the basis of ultimate capacities:

Table XII.

Product	Cc. 400 ppm. Water Softened
Quebracho-formaldehyde	700
Quebracho-sulphuric acid	1650
Bindex-acid sludge	1500

As stated in the section "Factors Affecting Practical Applications" (pp. 109-119), this is not conclusive; a more reliable indication of comparative quality is furnished by the operating Exchange Capacity and Salt Consumption per unit of hardness removed. In IVB3b this was determined for typical materials. The graph (Fig. 8) expressing the results shows that in the normal operating range (less than 10 lb. salt per cu. ft.) the Bindex-acid sludge and quebracho-acid sludge will remove from four to six times the amount of hardness per pound of salt as would be taken up by the quebracho-formaldehyde resin.

This demonstrates definitely the superiority of the acid-resinoid type of organolite.

A few other points of difference may be mentioned. In IVB2a it is noted that the quebracho-formaldehyde resin throws color (i.e., bleeds a brown color into treated water) and also is liable to mold growth, whereas the quebracho and Bindex acid resinoids do not. The bulk densities, i.e., the weight per cu. ft. of dry, granulated product of same mesh size, are about the same. The formaldehyde resin has the advantage as far as physical strength goes, for it is about as hard as gel zeolites, whereas the acid resinoids are somewhat softer. A quantitative determination of the resistance to abrasion has not yet been made. The effect of pH on the exchange capacity of acid sludge-Bindex was determined in IVB3a; analogous data was not determined for quebracho-formaldehyde, but it was ascertained that the lowest and highest pH values used in IVB3a did not increase the color throwing tendencies.

An interesting economic comparison is furnished by a consideration of approximate raw material costs. (The aliquot costs of labor, equipment, etc., may be assumed to be roughly the same for each of the products.) Based on costs as quoted by <u>Oil, Paint, and Drug Reporter</u> (86),

Quebracho extract, solid, 63%	4.0¢ per lb.
Formaldehyde, 37%	5.5¢ per lb.
Sulphuric acid, 66° Be	1.5¢ per lb.
Hydrochloric acid, 22° Be	2.25¢ per lb.

and private communications of Ellis-Foster Co.,

Acid sludge	about 0.1¢ per lb.
Hemlock sulphite liquor (Bindex)	2.25¢ per lb.

the costs may be calculated as in Table XIII.

Table XIII.

Constituent	Quebracho-Formaldehyde Wt., lb.	Quebracho-Formaldehyde Cost, ¢	Quebracho-Sulphuric Acid Wt., lb.	Quebracho-Sulphuric Acid Cost, ¢	Bindex-acid Sludge Wt., lb.	Bindex-acid Sludge Cost, ¢
Tannin	1	4.00	1	4.00	1	2.25
Acid	0.5	1.12	3	4.50	4	0.40
Aldehyde	2	11.00				
Total		16.12		8.50		2.65
Yield	0.9		1.6		3.0	
Cost per lb.		17.9		5.3		0.88

In summary it is apparent that the acid resinoids are superior to the phenolic resins on points of exchange capacity, salt consumption, economy, and other minor conditions of operation. There is little to choose between the best acid resinoids except on the basis of costs, where the Bindex-acid sludge material has the advantage of a raw material cost of less than a cent a pound.

Contrast of Organolites and Zeolites

In a sense this entire thesis is a comparison of organolites and zeolites. This presentation has been unavoidable and even desirable, because the present status of the zeolites provides the thread on which to hang the case of the organolites. In this section the two are contrasted and the relative advantages and disadvantages presented for the application in which they are competitive, namely, water softening. (The organolites are much more versatile than the zeolites, and the non-competitive uses will be presented subsequently.)

Comparing the zeolites with organolites, typified by Bindex-acid sludge, on the basis of Ultimate Exchange Values, we see from ID1a and IB2c that the organolite is about twice as good as the greensand zeolite, and the gel zeolite has about two and one-half times the capacity of the organolite. Here, again, the Operating Exchange Values are more indicative and may be compared by consulting Figure 8 accompanying IVB3b. Since the curve for gel zeolite was plotted from data given in the literature (123), direct conclusions must be cautiously drawn from it, since it may not fit the conditions under which the other curves were obtained. It would seem that when regenerating with about 4 lb. of salt per cu. ft., the organolite would compare favorably with the gel zeolite, but the slope of the zeolite curve is so steep a slight increase in salt would make a vast increase in calcium carbonate absorbed. It is therefore logical to conclude that gel zeolites have the advantage over organolites. The comparison with the greensand zeolite is decidedly in favor of the acid-resinoid, however. The hardness removed per pound of salt used in the range of 4 to 8 lb. of salt per cu. ft. is 50-75% greater for the acid sludge materials than for the greensand. Tests in quantity with a portable commercial size softener (IVB1a and -b) bear out laboratory determinations.

It will be remembered that the advantage of greensand zeolite over gel zeolite is that it is more resistant to aggressive waters. But even the greensand zeolites are not completely resistant; for all practical purposes the organolites are. For instance the effect of pH is nominal with Bindex-acid sludge as shown in IVB3a. In the pH range of 7 to 4 there is no variation in exchange capacity. On either side of this range the capacity increases directly with the pH value. The change of capacity with pH is similar to that of zeolites but not nearly so pronounced. Behrman and Gustafson (16) determined the decrease in capacity with a pH drop from 7.8 to 6.0 of greensand, high capacity greensand, and gel zeolite (under different conditions than used in IVB3a, however) and found percentage decreases of approximately 25%, 43% and 38%, respectively. The same p^H change produced only a 7% decrease in capacity of the investigated organolite. Beyond rather narrow limits (pH 6.5 to 8.0) (65), the capacity of zeolites falls off markedly with either an increase or decrease in pH (118); over the rather wide range of pH 11 to 2 the capacity drops 33% for the organolite. No tendency to disintegrate, dissolve, or throw color by the organolite was noticed in either the acid or alkaline conditions. Other conditions of raw water such as the carbon dioxide, silica, or aluminum content which influence the performance of zeolites (see "Factors Affecting Practical Applications," pp. 109-119) are without effect on organolites. It is evident that the organolites have important advantages over both classes of zeolites and combine to a certain extent the advantages of each zeolite over the other. A possible defect, however, is the lack of physical strength which renders the granules somewhat soft in contact with water. This sometimes occurs with gel zeolites as well. How serious this defect may be is not yet known; it is not thought to be excessive because the low specific gravity alleviates the possible abrasion of particles.

The matter of costs is also apparently favorable for the acid sludge-Bindex material. At present, for industrial installations, greensands sell for about $6.00 per cu. ft. and gel zeolites for about $11.00 per cu. ft. In cases of smaller installations the costs are greater. If it be assumed that the Bindex-acid sludge material is competing with a greensand on the same price basis, the organolite (bulk density, 45 lb. per cu. ft.) would be selling for 13.3¢ per lb. Since raw materials cost 0.88¢ per lb. (see p. 142), this gives a factor of 15 for ratio of selling price over material cost which should certainly prove ample for profitable manufacture. The similar factor for gel zeolite is 28. From the consumer's point of view, these figures indicate that the selling price might be less than that of the present zeolites.

The equipment for softening water with organolites would be substantially the same as for zeolites, since with the sodium chloride cycle no different chemical reactions take place. The differences between the types of zeolites limit industrial usage almost entirely to the more rugged greensand, while the synthetic is confined to small household installations. In the latter case, the zeolite is almost three times more effective than the organolite (IVB1a and -b), and, in spite of the enormous price differential, would probably not suffer greatly from competition by the organolite. The industrial picture, where the larger volume of zeolite is used, is quite different. An advantage over greensand which the higher capacity of the organolite reflects in the equipment is the smaller size apparatus necessary to handle given requirements. This, of course, pertains to newly designed softeners; substitution of media in already existing plants would increase capacity and require less frequent regenerations.

Behrman (<u>12</u>) divides the costs of zeolite softening systems into (1) initial installation; (2) fixed charges; and (3) operating expense. Naturally, no data are available specifically pertaining to organolites, but in a general way we may compare costs. (Statements of zeolite plant costs in some detail may be found in (43, 56, 130)). Since equipment would be either essentially the same or probably smaller, the initial installation costs would be likewise. Fixed charges includes such items as bond interest and amortization, overhead, and labor, and should compare in the same way as the initial installation cost. Operating expenses vary with the amount of water treated and include cost of salt, wash water, replacement of base exchange medium, and pumping. Salt and wash water (refer to pp. 111,112,113) would be smaller items with Bindex-acid sludge material; pumping costs might be less because a smaller filter bed would induce less head-loss; and replacement of medium might possibly be greater with the organolite. All things being equal, apparently the acid-resinoid has the economic advantage over greensand. Other things not being equal, the organolites possess technical advantages anyway where aggressive waters are encountered.

Regarding manufacture and processing of zeolites little is known of actual manufacturer's operations. Data available discuss them only in a general way and offer many alternative procedures (80). Furthermore, additional large-scale tests should be made on organolites (besides the IVA series) which were impossible under the writer's experimental set-up. The discussion of manufacture must therefore be brief for details would be mere conjecture.

Raw materials for the acid resinoid organolites are readily available. The amount, grade and cost of the supply of sulphuric acid are too well known to require more than a mention. Quebracho extract has been a staple import for many years (51) for the tanning industry; over one hundred million pounds per year have been imported for the last five years (95), so its supply seems ample. One oil company alone has available six tons of acid sludge per day (96). Bindex and other sulphite liquors are also produced in very large quantities. Thus, there is no apparent paucity of raw materials, and the demand by an organolite plant would probably cause no appreciable change in price level.

Equipment for manufacturing, say, acid sludge bindex, would probably be more troublesome and costly than for zeolites. The corrosive nature of the sludge (or sulphuric acid, if it be used), both concentrated and dilute (in the form of washings), would require resistant materials of construction. The disposal of acid wastes and sulphur dioxide fumes presents another problem. Because of the great increase of viscosity which occurs with the reaction between a wood extract and an acid, a powerful stirring device is necessary. The difficulties encountered in IVA2a and -b illustrate the dilemmas which are liable to arise. It seems probable that a rather large portion of the costs of manufacture would be allotted to equipment and processing costs. Actual labor costs would probably be low. The development of a definite detailed process remains for the future.

Efforts to obtain recent reliable information regarding the zeolite market were almost fruitless.

The Department of Commerce apparently ceased to publish such statistics since 1930. Naturally, manufacturers are reluctant to disclose private information, but it has been estimated that the number of industrial softeners operating in this country is about 30,000, and the number of household softeners about 220,000 (96).

Undoubtedly, quite a large market exists for base exchange water softeners. How much of this could be secured by organolites in the face of competition from tried and proved zeolites is problematical. Any commercial exploitation of organic base exchange media would advisedly be initiated in enterprises where emulation is less required. Some of these will be pointed out in the following sections.

Other Industrial Water Treatments

Acid Regeneration

A number of virgin fields exist where organolites might be applied, without fear of competition from zeolites, by taking advantage of their exceptional qualities. The first to be discussed is that arising from exploitation of the possibility of regeneration by acid instead of sodium chloride.

Hydrogen ions, of course, should base exchange the same as any other cation. Therefore hydrochloric acid may be theoretically substituted for sodium chloride as a regenerant. This can not be practically realized with zeolites, however, because they are decomposed and dissolved by the acid, the exchange capacity is lowered (118, 16), and zeolites may actually be incapable of exchanging hydrogen ions (61). But with organolites they theory becomes a fact.

The resins (e.g., IAla) and acid resinoids (IB series) are saturated with hydrogen ions as prepared. As noted in the fourth paragraph of IAla, the effluent from the first softening run is acid and must be neutralized before the hardness is determined. This is because the calcium ions have exchanged for the hydrogen ions; it is not caused by free acid remaining in the resin, this having been thoroughly flushed out with the distilled water. When the filter bed has become saturated with calcium ions, it may be regenerated with any acid whose anion constituent forms a reasonably soluble calcium salt. This is demonstrated in IIIB1a where dilute sulphuric acid is used as the regenerant.

On first consideration this may appear a foolish procedure, since the water is not truly softened, for the hydrogen ions in the effluent can precipitate insoluble fatty acids from soap. But further consideration will show that there exist several instances where such a treatment would be very valuable.

To digress for a moment, the expensive and destructive steam boiler explosions, caused by so-called "caustic embrittlement" of the boiler steel, have been an argument against softening water by the base exchange process for years. Natural waters containing carbonate or bicarbonate hardness, when softened with zeolites, yield an effluent which contains an equivalent amount of sodium carbonate or bicarbonate. According to an extensive investigation by F. G. Straub (114), caustic embrittlement is liable to occur in a boiler using such water. The process by which this is brought about is said to be:

(a) Waters containing sodium carbonate or sodium bicarbonate hydrolyze to sodium hydroxide at boiler temperatures and pressures.

(b) Although the proportion of caustic soda is small in the whole mass of boiler water, it reaches local high concentrations in capillary spaces between boiler plate joints, etc., because the alternate lowering and raising of pressure on the boiler forces liquid into the capillary, from which steam can escape but liquid can not.

(c) As the concentration of sodium hydroxide becomes sufficient (10% may cause embrittlement) in these spaces, it attacks the iron around the stressed regions (e.g., near rivets), the overvoltage being sufficient to form Fe_2O_3 with evolution of hydrogen. Because of the crystalline structure, the corrosion follows the interstices between the crystal granules of iron with a resultant failure.

The Bureau of Mines has recently shown that the presence of a minute amount of silica is also a necessary factor (98).

An additional objection to sodium bicarbonate water is voiced by the laundry trade because the small amount retained by fabrics changes to sodium carbonate during the ironing process and renders the starch yellow.

It is evident that if there were some way of eliminating the carbonates, zeolite-treated water could be safely used in boilers. Several cases are recorded where sulphuric acid has actually been added to such water to decompose the salts to sodium sulphate (which is said to be beneficial) and carbon dioxide (114). This, of course, is done with the added expense of acid and of equipment for such addition, with the danger of an excess which might be ruinous to the boiler and with the final result that the total solids are not reduced. It may have occurred to the reader that the whole trouble might be obviated by using the lime-soda process, which would remove the carbonates as the relatively insoluble calcium precipitate. This is actually done in many instances, but with the attendant disadvantages of the method (discussed on p. 134) coupled with the special calamity that the water cannot be completely softened; the cumulative effect is the deposition of scale in the boiler with the well known accompanying injuries (9, 55, 115, 116) which have inspired the introduction into the boiler of everything from a raw potato and a cup of treacle to sodium fluoride (99).

Herein lies a most important application of the organolites — they may be used to provide "zero hardness" water without the potential alkali content. For, when carbonate or bicarbonate hardness is removed by base exchange with an acid regenerated material, the effluent contains carbonic acid which spontaneously decomposes according to the familiar equation:

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

Coupled with this is the advantage of using a non-siliceous medium which precludes introduction of silica which might tend to bring about caustic embrittlement or cause a particularly troublesome and tenacious type of boiler scale. The process of acid regeneration is illustrated in IIIB1a.

The carbon dioxide may be removed from the water, if desired, by aeration, thereby actually eradicating the hardness salts, not merely nullifying them. This would be exceptionally effective on water such as supplied by the Great Lakes which contains about 120 ppm. temporary hardness, yielding almost the equivalent of a distilled water (91). If the water contains sulphate or chloride hardness, sulphuric or hydrochloric acid will occur in the effluent which would ordinarily have to be neutralized in some way before use. (Note in IIIB1d that there exists in the test water a non-carbonic acidity which is not removed by boiling. This was caused by using Montclair, N. J., tap water containing permanent hardness for preparing the test solution in IIIB1a.) Advantage might be taken of this situation by utilizing the rise in pH occurring when all the hydrogen ions have been exchanged to actuate an electrical device to shut off the flow of water, thus preventing over-running. From IIIB1c it is apparent that water containing both temporary and permanent hardness in certain proportions could be successfully treated by using a mixed regenerating solution. This would suffer the disadvantage that suitable water would not be delivered continuously, but the entire softened effluent from any one cycle would have to be mixed before use, for the first portions would be acidic and the last portions alkaline.

A related application offers successful treatment of waters possessing "negative hardness," i.e., alkaline or sodium bicarbonate waters. Here a neutralizing acid could be spontaneously and automatically liberated by an acid-regenerated organolite providing a palatable and useful water. IIIB1b illustrates this.

A recent technical development in lime-soda softening known as "recarbonation" suggests the possibility of using the carbon dioxide-containing water without aerating it. When water is softened with lime, especially in the cold process, the reaction is sluggish, and it is difficult to obtain an effluent of low non-carbonate hardness by using the theoretical amount of lime. Hence, "overtreatment" is resorted to, that is, an excess of lime is added which effectively removes the hardness but results in the presence of calcium hydroxide in the effluent. This is objectionable especially because of after-precipitation and formation of scale deposits in pipe lines, principally in hot water systems in domestic service and large buildings and also in feedwater heaters for boiler installations. This has been overcome by stabilization of the water with carbon dioxide (57). Present installations usually burn coke or other fuel and absorb the carbon dioxide formed in a diffuser or absorption tower. If it be deemed more economical to soften a given water by the lime process, it may be recarbonated by passing a water containing carbonates through an acid-regenerated organolite and combining the effluent containing carbon dioxide in solution with that from the lime process.

Water from acid regenerated organolite treatment would probably be useful in a variety of instances besides for boilers. The quality of being free of all metallic ions should prove of great value. It might replace the more expensive distilled water in some cases, e.g., for make-up in lead storage batteries.

A recent development in the technic of extracting Vitamin B_1 (which possesses a basic nature (134)) from leachings of rice polishings, brewers yeast, and wheat germ involves the use of a gel zeolite. The extraction is accomplished in an acid medium (pH 4), and the zeolite is given a preliminary acid wash (25). Inasmuch as the resistance to low pH is better in organolites than zeolites, the substitution of the former is suggested in Vitamin B_1 concentration process.

Anion Removal

In the last part of the section on "The Use of Synthetic Resins" (p. 29), the parallel between anion exchange and base exchange was presented. The anticipations of Adams and Holmes' work (3) have not been fulfilled, however. At least one recent review of the situation admits, "Resins made from aromatic bases exhibited considerable variations in the acid-exchange values according to methods of preparation and regeneration of the resins and the solutions used in determining the exchange value," (5). This is borne out by the writer's experiments. In IIIA1a and -b the experiments of Adams and Holmes with phenylenediamine were repeated. The absorption of chloride ion was small, and regeneration was unsatisfactory. The aniline-formaldehyde resin prepared with a basic catalyst (IIIA1c) was not applicable because of the solubility in dilute hydrochloric acid.

Since amine-aldehyde resins in general tend to be acid-soluble, it was thought that aminophenols might resinify by virtue of the phenolic group and yet be active through the amino group. It was found that p-aminophenol (IIIA2a) remained soluble, but m-aminophenol condensed with formaldehyde to produce a resin which was insoluble (IIIA2b). Even though this possessed a higher exchange capacity than the diamine material, its regeneration was indifferent. An interesting result in this respect is the use of neutral salts and acids for regeneration; Adams and Holmes apparently considered bases as necessary.

Another class of insoluble amino compounds consists of the vat dye-type of oxidized aniline derivatives. These are presented in IIIA3a-e and IIIA4a and -b. The dichromate oxidation product of aniline (IIIA3b) was the most successful, having a high initial exchange capacity for chloride ion; but here again regeneration produced a gradual decrease in capacity with each cycle. The use of other oxidizing agents (IIIA3c, d, and e) was unsatisfactory, as were also the products from homologs of aniline and related compounds (IIIA4a and -b).

Adams and Holmes suggested that proteins might prove useful as anion absorbants, but describe no experiments to substantiate the belief. On the basis of IIIA5a-d, where albumin, zein, casein, and blood were tried, it would seem that the proteins are inactive and also too water-sensitive to be of value.

From the experimental and published data in the present state, no definite conclusions as to value of such anion exchange materials can be drawn. Certainly the possibility of utilization exists and, although known results are discouraging, the problems may be solved in the near future. The solution may lie in a thorough investigation of the effect of pH, as the influence of this factor is apparently profound in anion absorption in soils (128).

A crying need is manifest in the great increase in literature on fluoride content of water supplies and its effect and removal. In 1931 it was experimentally proved that fluoride in drinking water was definitely the cause of endemic mottled tooth enamel (100, 131), which had been described as early as 1916. This disease takes the form of opaque spots or bands, usually on the upper teeth, the color and severity of which varies with the fluoride content of the water. As little as 1 ppm. may cause white spots which vary to yellow, brown or black as the fluorine rises to 2 or 4 ppm. or more. If the concentration is more than 12 ppm., the bones are apparently attacked. There are several districts in the United States and Canada where the safe limit of fluoride content is exceeded; a large proportion of the persons who have spent their childhood here (i.e., lived in the endemic regions during the period of tooth and bone formation) show the symptoms of mottled enamel. Three means have been used with indifferent success in attempts to lower or eliminate the fluorine content of such waters: overtreatment with lime in presence of magnesium (108), absorption by active alumina (119) and absorption by carbon at low pH (72). Each system has its particular disadvantages and incapacities. The writer had no success in fluoride removal when amino-resins, acid resinoid, and exhausted gel zeolite were used (IIIC1a). It was hoped that the latter, manganous and calcium zeolites, would form insoluble complexes with the fluorine, but to no avail. Perhaps, when the anion-exchange process is perfected, this problem may be solved.

Much furor was raised in this country and in England by the statement that "distilled" water might be prepared by filtering, for example, sea water successively through beds of acid-regenerated polyhydric phenol-formaldehyde resin and of alkali-regenerated amino-formaldehyde resin, for in this way the cations would be replaced by hydrogen and the anions by hydroxyl, with the result that the original solid content would be completely removed, leaving substantially pure water (76, 79). This is experimentally possible and leads to interesting speculation but is hardly commercially practical on the present knowledge of anion-exchange materials.

Other Ion Removal

Since Adams and Holmes (3) showed that their resins were selective in respect to various cations, it might be feasible to extract a special combination (i.e., one or more specific salts) which is deleterious in a given process. For this purpose an amphoteric substance (or one which would absorb both cations and anions) would be desirable, for then only one filter bed would be necessary. Attempts to produce such from aminophenols (IIIA2a and -b) by copolymerizing an amine and a phenol (IIID1a), from a naturally occurring nitrogen-containing product (IIID2a) and from an amino-alkyd resin (IC1a), were unsuccessful (see also p. 126).

Among the ions which are obnoxious in specific industries are iron and manganese. Laundry, paper making, dyeing, canning, and brewing processes must guard against the use of water bearing these elements, for they cause brown stains and general discoloration (33, 66, 102). The application of manganese zeolite (i.e., zeolite regenerated with potassium permanganate) has met with some success in their removal in many water treating plants (68). The absence of copper must be assured in rayon plants. Sulphates and nitrates should be kept to a minimum in sugar refining factories since their presence interferes with correct crystallization and tends to make the sugar deliquescent. Chlorides are troublesome in alcohol distilleries (102). Lead may constitute a hazard in water for human consumption (58, 88). It was demonstrated in IIBla that this may be absorbed effectively. A list of limits of concentration for a number of substances has been given by Babbitt and Doland (8). For the removal of each of these elements special processes have been proposed or are in use. In many cases this might be done more efficiently and economically if the indications given by Adams and Holmes (see Table II, p.25A) were developed by research to produce specially absorbent resins.

A similar outlet for organolites might be in the purification of metals and salts by selective absorption either of the desired substance or its impurities. From a brief canvass of metallurgical processes (69) it appears that copper might be recovered from an ammonia extract of low grade ores, lead separated from silver or zinc, zinc from cadmium, bismuth from lead, cobalt from nickel, or tungsten from tin, all of which separations are rather troublesome at present. The preparation and purification of salts with zeolites was mentioned a few years ago by Austerweil (6); organolites may widen this possibility by virtue of the great pH tolerance.

It is not claimed by the writer that the suggestions of the preceding paragraphs are all operable; they have been mentioned merely to indicate the scope of possible commercial applications. A further application of rather more definite promise is the recovery of valuable metals from industrial wastes. This has been given some experimental attention with respect to gold in Experiment Series IIA. When the research on organolites was first begun, the poison ivy plant was considered as a possible source of polyhydric phenol because of its content of irritating constituent, urushiol (50; 35, p. 1205). Although a resin made from extractives of the plant was ineffective for softening water (IA2e), it proved to be efficacious for absorbing gold (IIA1a). In IIA2a is given a list of other materials tried; of these, a quebracho-formaldehyde resin and chestnut-sulphuric acid resinoid were active. It was later found that a more expeditious procedure was to suspend a small amount of a finely powdered organolite in the gold solution for a few minutes. This sorbed all the gold, which could then be removed by filtering off the suspended material (IIA3a). A large number of substances were active by this method, but it is interesting to note that zeolite and charcoal were not. Evidently there is a special sort of an absorption here. It does not seem to be a case of true base exchange, for it does not follow the principle laid down by Austerweil (see pp. 103, -9). Since base exchange is an extraction phenomenon, substantially complete removal of a given cation is obtained only if the zeolite is treated with relatively small successive portions of water. This means that in actual application the liquid must be slowly percolated through the solid; if the material is dispersed in the entire volume of liquid, base exchange will not be complete. Therefore the fact that a small amount of solid <u>will</u> extract substantially all of the gold from a large amount of dilute solution shows that it is not an ordinary base exchange phenomenon. It is plausible that auric ions form some sort of a complex with the organolite, for when cyanide ions are present, thus eliminating free auric ions, the absorption does not take place (IIA3b). Further, the procedure is not applicable to ions other than gold (IIB2a). The contrast of the suspension method with the filter method in the case of lead is given in IIB1a and IIB2a.

IIA1a illustrates the practical application of the method. In a pen point manufacturing process all the waste water is treated with lime and a filter aid and filtered (96). This removes the particles of gold, silver, osmium, ruthenium, etc., coming from the grinding operations. Gold escaping from the pickling and cyanide plating baths is not recovered by this procedure. It is shown (IIA4a) that the suspension method recovers this gold completely; it could probably be fitted in the present salvage technic by destroying the cyanide in the waste water with sulphuric acid, adding the pulverized organolite with the lime, and removing both soluble and insoluble gold in one filtration. Since 2500 gallons of waste water are handled a day, a possible $234 per diem might be saved.

The old dream of extracting gold from sea water by using this method of course presented itself. Serious consideration is precluded by knowledge of the extremely small concentration of 5 to 10 milligrams of gold per cubic meter of water; Haber (48) has shown that the idea is economically impossible if not fantastic.

Patent Situation

The history of the patent situation covering the softening of water with zeolites is discussed by Hoover (54). Briefly, the litigation which took place and the circumstances which resulted were as follows: After the founding of the industry as outlined in the historical introduction (pp. 8-15), the Permutit Co., which owned the Gans patents, filed a number of suits charging infringements of Gans' 1916 patent which claimed an apparatus (not the zeolites themselves) capable of alternate regeneration and softening cycles. The Permutit Co. was finally upheld, but during the litigation they were forced to disclaim novelty to upward flow of water through zeolites. Seeking a loophole, several concerns continued the manufacture of softeners using the upflow principle. The Permutit Co. still had a claim which had been held valid by two Circuit Courts of Appeal reading on the removal of brine from the lowest point of the apparatus. The upflow softeners were constructed so that laterals were placed in the bottom and a header carried the spent brine out of the top of the softeners. On suit this was at first held to be subterfuge, and as a result several small companies were forced out of business and a few large ones were licensed to the extent of using upflow softeners. The last suit filed in this connection was eventually carried to the U. S. Supreme Court, and a decision invalidating the lowest point connection claim was upheld.

By this time (1937), of course, the Gans patent has expired. Nevertheless, the Permutit Co. and probably some other concerns undoubtedly have important apparatus patents. The extent to which these may cover organolite softeners is not determinable, because the exact details of an organolite softener have not yet been sufficiently worked out. Nevertheless these apparatus patents will eventually have to be considered. Furthermore, it is understood that the Permutit Co. has applications pending on their Zeokarb material, and they have undoubtedly protected themselves as regards apparatus utilizing acid regeneration.

References and patents relating to organic base exchange materials are sparse; they have been noted in various places in the thesis. The search covered all thirty volumes of chemical abstracts and the issued numbers of Volume 31 to October 1, 1937; the Official Gazette of the U. S. Patent Office for 1935 and 1936; and all the books available in local libraries. In addition references cited by patent office examiners on Ellis-Foster Co. applications, services of clipping and patent bureaus in Washington, D. C., and further references cited in any of the foregoing sources have covered the literature with some thoroughness. The writer's conclusions in view of known data are now given; it should be remembered they are his personal opinions, and that he does not profess to be a patent attorney.

Regarding the phenol-aldehyde resins, Adams and Holmes are undoubtedly the original inventors. They were the first to publish (3, 4) and have secured British and French patents. The United States patent (2,104,501) was issued January 4, 1938. It is difficult to see how the Kirkpatrick patent (63) can be of much value or indeed how it was even allowed; it is almost identical with the Adams and Holmes process and material, and the scope of the claims is very narrow.

In considering the acid resinoid type of organolite, the literature has already been reviewed in some detail on pages 15-22. Borrowman (<u>20</u>) first patented the use of humates to soften water in the United States and filed his application in 1927 the same year that Fischer and Fuchs (<u>40</u>) published the same discovery in Germany. Here the priority may be a matter of days, and it is not known whom to credit with the conception of the idea. Patents covering treatment of various substances with acids are of very recent issue, but Muller (<u>77</u>) prepared such materials before 1933 and determined their exchange capacities. The British patents 450,574 and -5 (filed under German convention date of April 13, 1934) claim treatment of lignite, coal, and the like with sulphuric acid or equivalent. The corresponding United States patents apparently have not issued, possibly being rejected over Borrowman because the materials produced by the disclosures are essentially humic acids. The French patents 778,922 (1935), 784,348 (1935), and 805,092 (1936), whose contents are revealed on page 21 probably come closest to being the acid-resinoid type, since they include starch and molasses as being suitable raw materials for treatment with sulphuric acid. It is not evident that they are considered base exchange media, however, but rather forms of activated carbon.

Among the other patents covering activated charcoals, that of Hunicke (58), who "removed gold from sea water" with carbon, and early British patent to Halse (49), who heats any cellulosic matter with sulphuric acid to obtain a decolorizing charcoal, might be argued to antedate the present process. But it has been shown (pp. 128 and 129 and the experiments there referred to) that acid resinoids are not carbon and that carbon itself is not active in the same way, and therefore it may be argued that no activated carbon disclosure antedates the acid-resinoid process.

The use of humus for water softening is not thought to be citable, for neither Borrowman (20) nor Tiger et al. (124) disclose or claim anything but lignite (brown coal) or modifications of it; the prior art here clearly knew of the base exchange powers of humus, so a patent for the use of it as a water softening medium might be held invalid for lack of invention. Certainly neither of the patentees hints of materials of the acid resinoid type.

Regarding one specific vegetable material used, namely, redwood bark, Finn (39) has patented a sulphuric acid reaction product for use as a gas mark absorbent. Since he does not disclose its use for water softening nor does he indicate that the material can be regenerated, it is not thought to have any bearing on the acid-resinoid applications. Apparently, then, the Ellis-Foster Co. owns the right to base exchange media made by treating water-soluble vegetable extracts with strong acids.

So far as is known, no United States patents have been granted for preparing base exchange materials by treatment of wood extracts by acids, which is essentially the process of preparing the investigated acid-resinoids. It is suspected, however, that there are in the neighborhood of about 15 applications pending in the Patent Office from several inventors. When and if these are allowed, and possible interferences settled, something definite may be known about the patent rights. The situation is in such a state of undetermined flux at present that no definite conclusions can be drawn.

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