

AN ABSTRACT OF THE THESIS OF

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Title: ----- A STUDY OF THE COAGULATION OF KRAFT EFFLUENT -----

----- BY SEA WATER -----

Abstract approved: -----

  
Frank D. Schaumburg

The coagulation of effluent from the kraft pulping and papermaking process was investigated. The amount of material coagulated from saline mixtures of the effluent is determined as a function of time, salinity, kraft effluent concentration, and mixture pH. Individual sources of salinity include sea water and several different solutions of salts containing some of the most prevalent elements in sea water.

It is found that sea water causes a limited coagulation of kraft effluent. Flocculation of an acid insoluble (Klason) lignin with cellulose fiber occurs. When all fiber is removed from the kraft effluent prior to combining with sea water, very small particles of the acid insoluble lignin are formed. Coagulation is essentially completed within 30 minutes after combining ingredients. A general increase

in the amount of material coagulated occurs with increases in mixture salinity and kraft effluent concentration.

Coagulation causes approximately a 20% increase in the amount of suspended solids settled from mixtures containing fiber. Mixture pH, carbon content, color and total alkalinity are unaffected by removal of coagulated material.

Pure solutions of sodium chloride, calcium chloride, and magnesium sulfate effect much greater coagulation of material than that which occurs with equivalent concentrations of these salts in sea water.

Coagulation of kraft effluent by sea water does not appear to offer a practical means for treating the waste.

A STUDY OF THE  
COAGULATION OF KRAFT EFFLUENT BY SEA WATER

by

Ben Neal Andrews

A THESIS

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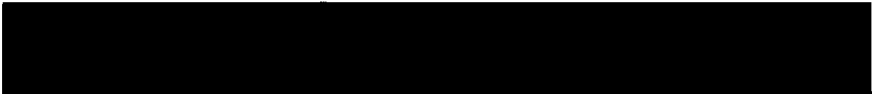
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## TABLE OF CONTENTS

I.	Introduction	1
	General	1
	Genesis of This Investigation	3
	Purpose of This Investigation	3
II.	Coagulation Theory	4
III.	Literature Review	8
	Characteristics of Sea Water and Kraft Waste	8
	Coagulation in Current Pulping Waste Treatment Practice	9
	Coagulation in Experimental Pulping Waste Treatment	12
IV.	Laboratory Investigation	20
	Qualitative Tests	20
	Quantitative Tests	27
	Scope	27
	Materials and Equipment	27
	Procedures	32
	Results and Discussion	34
	Characterization of Material Coagulated from Kraft Effluent by Sea Water	65
V.	Summary	67

TABLE OF CONTENTS (continued)

VI.	Conclusions	-----	71
VII.	Bibliography	-----	73

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Photomicrograph of floc particle	22
2. Retained material versus time (Sample 1)	36
3. Filtrate carbon versus time	38
4. Retained material versus time (Sample 1)	39
5. Retained material versus time (Sample 5)	39
6. Retained material and filtrate carbon versus salinity from sea water (Sample 2)	41
7. Retained material and filtrate carbon versus salinity from sea water (Sample 3)	42
8. Retained material and filtrate carbon versus salinity from sea water (Sample 4)	43
9. Retained material and filtrate carbon versus salinity from sea water (Sample 5)	44
10. Retained material and filtrate carbon versus salinity from sea water (Sample 5)	45
11. Retained material and filtrate carbon versus kraft effluent concentration (Sample 2)	47
12. Retained material and filtrate carbon versus kraft effluent concentration (Sample 2)	48
13. Retained material and filtrate carbon versus kraft effluent concentration (Sample 3)	49



## LIST OF FIGURES (Continued)

	<u>Page</u>
14. Retained material and filtrate carbon versus kraft effluent concentration (Sample 4)	50
15. Retained material and filtrate carbon versus kraft effluent concentration (Sample 5)	51
16. Retained material and filtrate carbon versus kraft effluent concentration (Sample 5)	52
17. Retained material and filtrate carbon versus salinity from sodium chloride solution	54
18. Retained material and filtrate carbon versus salinity from calcium chloride solution	55
19. Retained material and filtrate carbon versus salinity from magnesium sulfate solution	56
20. Retained material and filtrate carbon versus kraft effluent concentration	62
21. Retained material and filtrate carbon versus pH	64

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Kraft effluent - composite sample characteristics	28

# A STUDY OF THE COAGULATION OF KRAFT EFFLUENT BY SEA WATER

## INTRODUCTION

### General

The kraft pulping process is one method used in obtaining cellulose fibers from wood. Separation of the cellulose from the remainder of the wood is done by digesting wood chips in a cooking liquor at elevated temperature and pressure. Differences in the ability of the various components of wood to enter into hydrolysis reactions is the basis of the process. Cellulose is the least hydrolyzed and is left after the other components of wood have reacted and become dissolved or suspended in the alkaline cooking liquor.

Compounds of sodium constitute the active chemicals in the cooking liquor. Sodium hydroxide and sodium sulfide are the principal chemicals used. Sodium carbonate, sodium sulfate and sodium thiosulfate are also present in incidental amounts. A high percentage, 90% or greater, of chemical recovery is characteristic of the kraft process. Chemical recovery is accomplished by concentrating and incinerating the used cooking liquor.

Effluents from a kraft mill contribute significantly

to the pollution load of the receiving water. Waste water discharges of 13 - 30,000 gallons per ton of unbleached pulp produced are common. Fifteen tons per day of foreign material carried in the effluent can be expected from a modern mill having a capacity of 500 tons of unbleached pulp per day. Principle sources of waste effluents originating in a mill include accidental spills or leaks of the cooking liquor, evaporator condensates, and water used in pulp washing. If papermaking is done at the same site as the pulping, the paper machine represents another source of effluent. The composite effluent from these sources is a coffee-colored liquid containing a considerable amount of visible particulate material and has the distinctive smell of a kraft mill. Variable amounts of most of the constituents of wood remaining after removing cellulose are present in the mill effluent. Included are hemicelluloses, lignin, resins, fats and waxes. In addition, cellulose fibers, bits of wood, bark, glue, starch and filler material may be included as suspended matter. Trace amounts of chemicals contained in the cooking liquor will also be present.

A detailed description of the kraft pulping process is outlined by Kleinert (1965). Effluents from the process are characterized by Nemerow (1963) and Rudolfs (1953).

### Genesis of This Investigation

During an earlier investigation concerned with the degradation of kraft pulping wastes in estuarine waters, a "flocculation phenomenon" was observed by O'Neal (1966) after kraft effluent and sea water were mixed together. Flocculation occurred in various mixtures of sea water, fresh water and glass wool-filtered kraft effluent. A typical mixture consisted of enough sea water to contribute a salinity of 25 parts per thousand, fresh water to adjust the salinity, 10% by volume of kraft effluent and 1% by volume of a sea water medium containing biological seed. Floc appeared within the initial one-half hour after combining the ingredients. Aggregation of particles was observed to continue for several hours and settling time decreased as particle size increased.

### Purpose of This Investigation

An evaluation of the amount and character of the "flocculent material" together with the associated causative factors were primary goals of this research. Reduction by the flocculation of oxygen-consuming materials, suspended solids, dissolved matter, and color in effluents discharged to receiving waters was of interest as a possible treatment mechanism for kraft wastes.

## COAGULATION THEORY

Many waste waters, including kraft effluent, exist as sols wherein a solid phase is dispersed in a liquid phase. In lyophilic sols the dispersed phase exhibits an affinity for the dispersion liquid. Lyophobic sols have a repulsion between phases. If the dispersion medium is water the terms hydrophilic and hydrophobic are applied.

When the dispersed phase is colloidal in size, a sol has peculiar characteristics different from either coarse suspensions or true solutions. Interparticle electrokinetic repulsive forces, van der Waals attractive forces, hydration, and molecular bombardment experienced by the colloids, together with their tremendous surface to mass ratios, are responsible for these characteristics.

Colloids are particles of material ranging from about one millimicron to one micron in size. They vary in shape from near spherical to flat linear forms. Most colloids possess an electric charge, which is usually negative on natural materials. The charge on the particle gives rise to a peripheral layer of concentrated opposite charge due to ionic attraction and this in turn to a more diffuse layer of charge which blends gradually to the neutral potential of the surrounding liquid. The concentrated peripheral layer of charge is known as the Stern layer and

is more or less permanently associated with the particle. Movement of the colloid develops thru a plane of sliding at the interface of the Stern layer and the diffuse layer. The electric potential between this interface and the surrounding liquid is known as the zeta potential, the value of which is specific for a particular colloid.

The dispersed colloidal phase of a sol is subject to two stabilizing influences. These are the mutual repulsion of particles as measured by the zeta potential and hydration by water which forms a shell around the particle. Together with movement due to molecular bombardment by molecules of the dispersion liquid and thermal currents, mutual repulsion and hydration tend to prevent coalescence thru van der Waals attraction and settlement by gravity.

Coagulation is the process of removal of a dispersed phase from the dispersion medium through the coalescence of particles into aggregates of sufficient size such that sedimentation takes place at a faster rate than would occur otherwise. Usual applications are limited to hydrophobic sols because coacervation to destroy hydrated layers is expensive. Bringing particles into proximity sufficient for van der Waals forces to act is accomplished by either imparting energy to the particles or lowering the zeta potential. Heating, cooling and addition of charged particles are methods used in accomplishing these changes. Addition

of metal salts, principally of iron and aluminum, which react with water to form separate flocs that settle and screen out suspended material is another method of coagulation.

Charged particles in the form of ions differ greatly in coagulation effect. The Schulze-Hardy rule relates that bivalent ions have 20 to 80 times the flocculating power of univalent ions and that trivalent ions have 10 to 100 times that of bivalent ions.

Burbank (1963) describes the treatment of waste water by lowering of zeta potentials with cationic polyelectrolytes and activated silica. Suspended solids removals of up to 90% are cited. Hydrophobic colloids with adsorbed hydrophilic molecules are said to be prevented from flocculating even at zero zeta potential because van der Waals attractive forces cannot act due to the hydrated layers surrounding the hydrophilic molecules.

The charged and hydrated condition of hydrophilic sols are discussed by Jacobson and Schmut (1964). Requirements for electric discharge and dehydration prior to coagulation are noted. Lyophobic sols are said to respond by coagulating upon addition of small amounts of electrolytes.

The application in the paper industry of zeta potential measurement and adjustment are discussed by Schmut (1964).

Riddick (1961) divides turbidity into two fractions.

A coarse fraction has particles with diameters of one millimeter to one micron and a fine fraction contains particles with diameters of one micron to one-thousandth of a micron. Bacterial cells have zeta potentials ranging from 0 to -40 millivolts.



## LITERATURE REVIEW

The review of literature is presented under three subdivisions; (1) Characteristics of Sea Water and Kraft Waste, (2) Coagulation in Current Pulping Waste Treatment Practice, (3) Coagulation in Experimental Pulping Waste Treatment.

### Characteristics of Sea Water and Kraft Waste

The composition of sea water as given in the Handbook of Chemistry and Physics (1960) is;

<u>Element</u>	<u>Concentration ppm by weight</u>	<u>Element</u>	<u>Concentration ppm by weight</u>
Cl	18,980	K	380
Na	10,561	Br	65
Mg	1,272	C(inorganic)	28
S	884	Sr	13
Ca	400	plus traces of several other elements	

Woodard and Etzel (1965) characterize the effluent from the kraft pulping process as a lyophilic colloidal system with large lignin polymers held in suspension by solvating forces of water. A hydrated water layer about each colloid prevents coalescence and coagulation of lignin with other colloids in suspension. Jacobson and Schmut (1964) identify common colloidal materials in pulping

wastes as lignin, resin, pitch, cellulose fines and matter initially included in the process water. Paper machine furnishes<sup>1</sup> and white water are said to contribute colloids of glue, rosin, dye pigment, filler materials and wet-strength resins. Significant variation in colloidal composition of wastes from the paper industry is reported by Schmut (1964).

On the basis of electric charge possessed by the suspended colloids in kraft waste Woodard and Etzel have identified two major fractions. Electrophoresis studies revealed a migration of the larger fraction toward the negative pole at a pH above 2.1, indicating a positive charge on these particles. The smaller fraction exhibited the usual behavior shown by colloids of natural material by migrating toward the positive pole at a pH above 5.2. All mixtures of kraft pulping wastes and sea water may be expected to have values above the two mentioned.

#### Coagulation in Current Pulping Waste Treatment Practice

Treatment of wastes has not been universally practiced in the paper industry. Gehm and Lardieri (1956) made a survey of 180 paper mills in the U.S. of which 78 were

1. "Furnish" is a term used in the papermaking industry for the slurry of cellulose fiber and additives which comprises the raw material transformed into paper by the papermaking machine.

kraft mills accounting for 75% of the pulp production in this country. It was found that 55% of all mills surveyed had waste treatment facilities. Mechanical and biological methods were used in the majority of cases. As late as 1952 it was reported (Moggio, 1952) that, with one exception, chemical treatment had never proceeded beyond the laboratory stage. The exception involved a southern kraft mill which installed a lime treatment process based upon experimental results obtained at Louisiana State University.

In early attempts at using clarifiers in chemical treatment of kraft waste, Gehm and Lardieri say that activated silica and alum were the most commonly used coagulants. Up to 90% removal of suspended solids was attained. Glue was described as being used to coagulate white water.

The use of ferric chloride, ferric sulfate, and aluminum sulfate to coagulate board mill wastes from a plant where pulp production was not practiced is reported by Quirk (1958). Effectiveness in coagulation was, in increasing order, (1) ferric chloride, (2) aluminum sulfate, (3) ferric sulfate. Organic polyelectrolytes, activated silica and clay were used to aid precipitation. Coagulant doses of 70 ppm removed 100% of the suspended solids.

Ockershausen (1959) outlined the steps in coagulation of pulping wastes as;

1. neutralizing the negative zeta potential

2. formation of micro flocs

3. floc growth through adsorption phenomenon

Alkalinity was cited as a hindrance to coagulation. A 92% removal of suspended solids in kraft waste by the use of aluminum sulfate or lime was obtained. This was 17% above that obtained by sedimentation alone.

Pôbis' (1964) describes the removal of color from kraft liquor with the use of hydrated alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ). The waste liquor involved was from a kraft mill with a black liquor recovery efficiency of 70%. This is a low efficiency when compared to modern kraft mills in the U.S. and would result in effluents considerably stronger than are normal from plants in this country. Optimum treatment was obtained within a pH range of 5 - 6.2 with a dosage of 26 mg Al per 100 mg lignin. Reductions of 48% in 5-day BOD, 72.2% in COD and 95.3% in lignin content resulted from this treatment. Color was removed and foaming reduced. Large volumes of sludges were produced which were difficult to dewater.

Alum treatment was related by Murphy and Gregory (1964) as being successful in removal of color from effluent from the washing of chlorine bleached kraft pulp. Practical limitation of the method was due to difficulty of dewatering the sludge formed. Filtering was not thought to be feasible and centrifuging was uneconomical.

Růžicková (1965) describes up to a 99% removal of suspended solids from paper machine waste water by coagulation with activated silicate and alum. Coagulation of pulping wastes with  $\text{FeSO}_4$  in an alkaline medium resulted in reductions of 68.3% in COD, 89.4% in 5-day BOD and 95.4% in lignosulfonic acid.

Cationic and cationic-anionic polyelectrolytes used in dosages of 20 mg/l in treating paperboard mill waste water containing 550 mg/l of total solids resulted in 50-81% reduction in suspended matter. (Leszczynske and Skwara, 1965).

#### Coagulation in Experimental Pulping Waste Treatment

Experimental methods for chemical treatment of kraft mill effluents have been under examination in laboratories since soon after World War II. Numerous coagulants have been tried. Among early attempts were those which used alum and iron salts in a similar manner to that used in water treatment.

Moggio (1952) reports voluminous sludge, low in solids, resulting from an alum dosage of 1500 lbs/MG of waste effluent. Another method used barium alumina silicate with alum. A dosage of 2200 lbs/MG of alum followed by 5600 lbs/MG of the barium compound resulted in a supernatant free of color, organic matter, magnesium, calcium and sulfates. Without

the alum, 9600 lbs/MG of the barium compound was required to remove the color. The addition of sulphuric acid to kraft effluent also resulted in separation of material. Dosages of 740 - 800 lbs/MG resulted in 11-71% reductions in oxygen demand<sup>2</sup> by the effluents and 4500-6000 lbs of 66°Be H<sub>2</sub>SO<sub>4</sub> per million gallons of effluent were required for complete color removal. Results of other tests are as follows:

<u>Dosage</u>	<u>Results</u>
1600-5600 lbs/MG H <sub>2</sub> SO <sub>4</sub> plus 1600-3200 lbs/MG Alum	42-88% reduction in O <sub>2</sub> demand
1600-8000 lbs/MG Alum	32-85% reduction in O <sub>2</sub> demand
800 lbs/MG Lime	21% reduction in O <sub>2</sub> demand

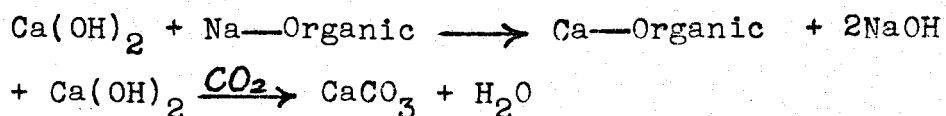
Char, clay, activated carbons, activated silica, ferric chloride, chlorinated copperas, phosphoric acid and waste pickle liquor were other compounds listed as having been tested experimentally for color and/or BOD removal. The general conclusion was that none of the above materials offered an economical means of waste treatment. Large quantities of gelatinous sludges were produced which were difficult to dewater even by vacuum filter or centrifuge.

Research extending over a period of ten years at

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2. It is not specified as to whether biological or chemical oxygen demand was altered.

Louisiana State University led to the development of a method for removing most of the color and suspended material from kraft mill waste water. (Herbert and Berger, 1960), (Moggio, 1953) This research showed that the brown color of the kraft waste is due to lignins and tannins dissolved during pulping. A small amount of organic matter was found to produce a pronounced color. A color-to-organic-matter ratio of 16:1 is reported, with color expressed in ppm<sup>3</sup>. Lignin was found to be precipitated by a number of materials, including lime, sulphuric acid and alum. Lime was concluded to be the best color precipitator. Initial lime dosages of 1000-1500 ppm were increased to 9000-28,000 ppm in the final method. The final method involved reacting the entire lime requirement of the mill with the pulping effluent. Resulting sludges were more easily dewatered than those obtained with minimal dosages. Calcium carbonate was identified as the primary precipitate which removed all color and up to 50% of the BOD. Vacuum filtration was used successfully in dewatering the sludge. The following reaction was proposed for the process:



A variation to the above method was evolved from this

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3. The account does not make clear the basis for reporting color in ppm.

research effort. (National Council, 1958) Color was almost completely removed from kraft pulping effluent upon filtration through hydrated lime beds as thin as 1/16 of an inch. The colored material collected at the surface of the bed and could be scraped away as a comparatively dry film. The lime underneath remained uncolored. It was theorized that the colored material reacted with the hydrated lime at the bed surface to form a crystal lattice of sufficient size or peculiar structure to prevent its penetration of the bed surface. The large size of lignin molecules, which account for most of the color of kraft waste, was cited as a plausible reason for a possible complex being formed by lignin and calcium. Beds of finely divided limestone and silica did not exhibit the color retention.

Polyvalent metal ions assist in the flocculation and precipitation of pitch. (Jacobson and Schmut) The cations are said to act by increasing the zeta potential of pitch colloids to near zero. Calcium and magnesium were effective in pitch precipitation at pH 6.0 and above.

Woodard and Etzel found that after coacervation with acetone in variable amounts, metal cations were effective in coagulating pulping wastes. Tests were made using volumes of acetone which in some instances were as large as the volume of waste being treated. In removing color the effectiveness of several cations, in increasing order,



was  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and for anions was  $\text{CH}_3\text{COO}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ . The effectiveness of all of these ions increased with pH and up to 90% color removal was attained by increasing the pH of samples to above 11.0. Color in kraft waste was found to obey Beer's Law.

In the same study the possibility of color removal being the result of a salting out process was investigated by adding several amounts of sodium chloride to samples of waste liquor and then raising the pH of the mixture to 13.5. No color removal due to the sodium chloride occurred until an amount greater than 25 g/l was added. Removal of additional lignin thereafter was attributed to a salting out mechanism and essentially complete color removal was attained at a level of 40 g/l of added sodium chloride. Most of the colored material was identified as sulfonated lignin. This material was thought to undergo an ion exchange of metal cations for hydrogen ions. The remainder of the colored material consisted of lignin degradation products exhibiting properties of an organic colloid having an isoelectric pH of 5.2.

Soluble calcium salts and milk of lime were shown by Uhari (1963) to precipitate resin and fatty acids as calcium salts from black liquor. The resin and fatty acids were found to be responsible for foaming which causes difficulties in the filtering of black liquor.

Schmut found polyvalent ions and alkaline earths to be effective in the agglomeration and precipitation of material from pulping wastes.

An outline of the results which may be expected with the use of polyelectrolytes in treating wastes of the paper industry is given by Follet and Gehm (1966). A great number of these materials have been tested, many of which are identified by trade names. Due to flocculation with polyelectrolytes, an 8% increase in suspended solids removal from boardmill wastes resulted. This represented an average of results of tests with 9 electrolytes on 12 samples of boardmill effluent. The dosage was 1 mg of polyelectrolyte per liter of effluent treated. Dosages of 2-4 mg/l were required on deinking wastes and white water and no flocculation occurred with smaller amounts. The treatment increased settling rates up to 40%.

Lignins have been identified as surface active agents by McCormick and Berger (1964). The use of the surface active property was tested in connection with foam separation of lignin from kraft effluents. Also reported is the use of cationic surfactants to complex or attract the anionic lignins and thereby cause separation. Of approximately 30 cationic surfactants tested, only Ammonyx LDA failed to precipitate lignin.

Separation of lignin from waste liquor by methods using

elevated temperatures and pressures together with pH adjustments has been accomplished by Ball and Vardell (1961). In one method black liquor of 30% solids concentration is carbonated to a pH of 9.7 and heated to 141.5°C under a pressure of 150 psi gage. The lignin is separated as a viscous lower layer. Another method utilizes a mineral acid to precipitate colloidal lignin from black liquor. The colloidal lignin is then coagulated by heating to 79-104°C followed by cooling to 60°C. Separation is completed by filtration.

The use of adsorbents in removal of lignin and accompanying color from kraft waste waters has been reported by Murphy and Gregory (1964). A 20-to-60 mesh clay (Florite), as obtained from the Floridin Company of Tallahassee, Florida, increased light transmittance by 90%. Adsorption of the color producing material onto the clay particles was credited as being the mechanism of the color removal.

Effective removal of the colored fraction in kraft waste by adsorption onto sediment naturally carried by receiving waters is reported by Nelson (1963). It was found that the color adsorption occurs onto a wide variety of clay materials and that, under natural conditions, river sediment never became saturated by the kraft effluent. This report also suggests a natural reaction between effluent substances and dissolved chemicals as a possible

source of precipitation or floc formation. Such a reaction was thought to be especially likely in marine or brackish waters.

## LABORATORY INVESTIGATION

Qualitative Tests

Initial laboratory tests were made to observe the appearance and growth of floc as described by O'Neal (1966). Mixtures consisted of kraft effluent from a grab sample, sea water and distilled water. As outlined by O'Neal, kraft effluent concentrations of 7% and 10% by volume and salinities of 15 ppt and 25 ppt by weight were used. Since O'Neal reported that the amount of floc seemed to increase with effluent concentration and salinity, mixtures of 15% and 20% effluent in undiluted sea water were also evaluated.

Difficulties were experienced at first in producing the expected flocculation. This was perhaps due to non-detection of the very small-sized floc sometimes formed, as described by O'Neal. Subsequent successful tests revealed that much of this initial difficulty may also have been due to a weak effluent sample having been obtained by grab sampling or to aging of the sample.

O'Neal related that the floc appeared within 30 minutes after mixing the ingredients and therefore biological activity was ruled out as a possible causative factor. However, due to the initial difficulty in producing flocculation, an acclimated biological seed was included in later test mixtures so that all the ingredients utilized by

O'Neal would be present.

Floc formation occurred when glass wool-filtered kraft effluent from a composite sample was mixed with glass wool-filtered sea water. A tan colored, feathery, fragile floc appeared in each of the following mixtures.

<u>Ingredient</u>	<u>Mixture</u>					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
kraft effluent (percent by volume)	7	10	7	10	15	20
salinity from sea water (ppt by weight)	22.3	22.3	13.4	13.4	26.2	24.6
distilled water (percent by volume)	20.5	17.5	49.1	46.1	0	0
biological seed in kraft effluent and sea water medium (percent by volume)	1	1	1	1	1	1

Figure 1 is a photomicrograph of a particle of flocculated material. The floc consists of a mesh of cellulose fibers onto which a fine-grained, tan material has agglomerated. The fine-grained tan material was possibly coagulated from the kraft effluent by the sea water and subsequently adsorbed onto or screened from suspension by frameworks of fibers.





Figure 1. Photomicrograph of floc particle  
Magnification 40X

In other tests the approximate time required for flocculation to occur and the effect of prefiltering the kraft effluent and sea water through glass wool before mixing were evaluated. The floc began to appear in approximately 15 minutes after combining the ingredients and appeared to grow in number and size with time. It was observed that mixtures which contained unfiltered ingredients seemed to have a slightly higher concentration of floc. The growth of floc with time and the increased concentration of floc obtained with unfiltered ingredients were probably due to floc formation being the result of a random encounter of fine-sized coagulated material with fibers. In an occasional mixture flocculation did not readily occur despite the presence of an abundance of visible particulate material. If stirring was continued

for several hours, flocculation did take place to some extent. Formation of fiber meshes which form the framework of the floc evidently took longer in some cases.

The individual significance of sea water, kraft effluent and biological seed to the floc formation was demonstrated by tests of coagulation in mixtures containing the following ingredients.

<u>Ingredient</u>	<u>1</u>	<u>2</u>	<u>3</u>
kraft effluent (Percent by volume)	15	15	0
salinity (ppt by weight)	0	26.2	26.2
distilled water (percent by volume)	84	0	15
biological seed in a kraft effluent and sea water medium (percent by volume)	1	0	1

Flocculation occurred in mixture 2 but not in mixtures 1 or 3. Mixture 2 lacked biological seed and therefore the occurrence of flocculation established that the seed was not a requirement for the coagulation. Either the kraft effluent or sea water was deleted from mixtures 1 and 3 and the absence of flocculation established the requirement for these ingredients to the coagulation.

It appeared that the fine-grained, tan colored material was the primary product of the coagulation of kraft waste by sea water. A series of tests was initiated to determine the effect of removing the fibers and various amounts of smaller sized material by filtering the kraft effluent and



sea water through media of different porosity. Glass wool was used as a coarse filtering media and Watman No. 1 filter paper as a fine filter in the mixtures tabulated below.

These mixtures all consisted of 20% kraft effluent, by volume, and sea water.

<u>Mixture</u>	<u>Kraft effluent</u>	<u>Sea water</u>
1	unfiltered	unfiltered
2	Watman #1	Watman #1
3	unfiltered	Watman #1
4	Watman #1	unfiltered
5	glass wool	glass wool
6	glass wool	unfiltered

High concentrations of floc formed in mixtures 1 and 3.

A great deal of floc appeared in mixtures 5 and 6 but was smaller in size and concentration than 1 or 3. In mixtures 2 and 4 a relatively small amount of fine-grained, tan-colored material resembling a fine precipitate rather than floc appeared. This was probably the same type of material which aggregated with meshes of fiber to produce the floc appearing in mixtures 1, 3, 5, and 6.

A similar test in which glass wool was used as coarse filtering media, Watman #40 as an intermediate, and Watman #42 as a fine media gave essentially the same results. The amount and size of coagulated material decreased with a

decrease in pore size of ingredient-filtering material.

The formation of fine grains of tan-colored material in mixtures of kraft effluent and sea water, both of which had been prefiltered through a 0.45 micron Millipore filter membrane, gave definite indication that either dissolved or colloidal material was involved in the coagulation. Particles of coagulated material in such mixtures were very fine and difficult to observe visually but resulted in a small deposit on the bottom of the containing vessel after quiescent standing for several hours.

In mixtures of ingredients from which all fiber had been removed, the fine material did not form floc large enough to cause significant settlement from suspension. The addition to such mixtures of small amounts of flocculated material which had previously been collected and dried or portions of other mixtures containing floc in suspension seemed to aid in flocculating some of the fine material.

Observations were made of the effect of heating ingredients to about 80°C before combining them. It appeared that heating aided in coagulation of mixtures containing unfiltered ingredients but had no noticeable effect upon those containing filtered ingredients. During solids determinations it was noticed that several large flocs of brown material developed as the temperature increased in evaporating dishes containing unfiltered effluent. Distinct spots

in the dried residue resulted from these floc. Gas was evolved from these spots upon the addition of strong mineral acid. Identification of sodium as a primary constituent of the residue by the precipitation of sodium zinc uranyl acetate after the addition of a solution of zinc uranyl acetate indicated that the floc contained sodium carbonate or bicarbonate.

## QUANTITATIVE TESTS

### Scope

A series of tests was undertaken to quantitatively measure the amount and determine the nature of material coagulated in kraft effluent under different conditions.

Measurements were made of variations in the amount of material coagulated versus time, salinity, kraft effluent concentration, and pH as independent variables. Individual sources of salinity included either sea water or one of several different solutions of salts containing some of the most prevalent elements in sea water. Removal of carbon with coagulated material was monitored.

The material separated from kraft effluent was examined for lignin, nitrogen, sodium, magnesium, carbonate or bicarbonate and solubility in organic liquids.

### Materials and Equipment

Characteristics of several samples of kraft effluent used in tests are listed in Table 1. Within a particular category, such as COD, values differ considerably between samples. According to mill personnel who make regular determinations of effluent properties, large variations are normal. Total solids values in Table 1 are very low compared to typical values reported by Nemerow (1963).

\* Includes Sample 1

\* Includes Sample 6

Sample	1	2	3	4	5	6	Mean	Std. Dev.
COD = mg/l	770	464	459	414	506	486	466 516*	31 117*
Percent of Std.Recovered - %	100	100	96	96	100	97	-	-
Total Solids - mg/l	853	474	601	546	546	545	542 594*	40 121*
Percent Volatile - %	48	38	39	40	42	40	41	3
Dissolved Solids - mg/l	-	423	512	443	461	443	456	30
Percent Volatile - %	-	34	34	32	36	29	33	2.4
Suspended Solids - mg/l	-	51	89	103	85	102	86	19
Settleable Solids -ml/l after 1 hr.	0.9	-	1.8	2.9	2.9	6.4	2.5 3.5*	0.6 1.7*
2 hr.	-	-	3.0	3.9	3.9	8.5	3.6 4.8*	0.4 2.2*
Phenolphthalein Alkalinity -mg/l as CaCO <sub>3</sub>	67	35	58	32	31	32	38	10
Total Alkalinity -mg/l as CaCO <sub>3</sub>	155	79	127	90	87	86	94	17
pH	10.5	10.0	10.1	9.8	9.8	9.8	9.9	0.3

Table I. Kraft Effluent - Composite Sample Characteristics

Suspended solids are close to typical minimum values. Total alkalinities are slightly below the typical minimum. Phenolphthalein alkalinities and pH values are somewhat higher than those listed as typical. Chemical recovery of 95% or better and very efficient in-plant procedures to reduce material losses through spills and other operational errors account for the generally low solids content of the effluent. A greater than normal loss of sodium hydroxide in the mill's process is indicated by high phenolphthalein alkalinity and pH values.

Douglas fir and a small amount of pine are the principal species of wood used as a source of cellulose at the mill where the kraft effluent was obtained. The plant produces an unbleached kraft pulp which is used at the site in the manufacture of brown paper. No slimicides are used in the papermaking process. Machine white water is recycled to reduce the amount of suspended material entering the waste stream.

A Parshall flume located on the plant's effluent line was the site selected for a sampling station. The 24-hour composite samples were obtained with the use of a Sigma-motor articulating-finger pump. Each sample was held in a collection container inside a refrigerator during the sampling period. Immediate cooling to a temperature of 5° to 10°C retarded biological growth and helped to preserve the

chemical nature of the sample. The sample was kept refrigerated until used in tests.

Sea water included as a basic ingredient in test mixtures was obtained from a pumping intake line at the dock near the Oregon State University Marine Science Laboratory located in the vicinity of Newport, Oregon. Pumping was done during high slack tide in order to obtain water with properties as similar as possible to those of the open sea. The sea water was transported in a barrel lined with polyethylene sheeting and fitted with a water-tight lid. Refrigeration to near  $5^{\circ}\text{C}$  aided in preserving water properties.

Salinity of the sea water was determined from measurements of density (with a glass hydrometer) and temperature. This data was used with U.S. Department of Commerce Sea Water Temperature and Density Reduction Tables by Zerbe and Taylor (1953). A calculated value of 31.2 ppt was consistently obtained, which is somewhat less than the general world-wide open sea salinity of approximately 35 ppt.

A Barnstead still was the source of distilled water. This water left no measureable residue upon evaporation, showed no ammonia upon testing with Nessler's reagent and contained 5 to 6 mg/l of total carbon.

Materials and reagents used in making standard physical and chemical tests conformed to those prescribed in

Standard Methods for the Examination of Water and Wastewater by the American Public Health Association (1966).

The equipment used in the laboratory investigation consisted of items standard to a sanitary engineering laboratory. A Phipps and Bird laboratory stirrer provided uniform mixing of the ingredients used in the coagulation tests. This instrument has six stirring stations monitored by a common tachometer. Samples were contained in 600 ml beakers and mixtures were illuminated by a fluorescent light mounted behind the stirrer.

A Beckman Model IR315 Infrared Analyzer was used to determine carbon content of filtrates. Representative values for carbon content of mixture ingredients are:

<u>Ingredient</u>	<u>Organic carbon</u>	<u>Inorganic carbon</u>
Kraft effluent	90 mg/l	15 mg/l
Sea water	2	23
Distilled water	5	0

The values do not include carbon in particles larger than those which will pass through a Hamilton #702 syringe needle as attached to the .025 ml injection syringe used with the carbon analyzer.

Gravimetric measurements were made with a Mettler balance sensitive to 0.1 milligram.

Filtering media included glass wool and Watman Grade



GF/C glass fiber pads. These pads are available in diameters as large as 9 cm and may be brought to constant weight and used in both filtering and igniting procedures. A weight obtained after heating for 2 hours at 538°C was found to be applicable at 103°C also. In all volatility determinations with these pads 538°C was used. Higher temperatures destroyed the pads due to uneven heating in the muffle furnace. A Hirsch funnel was found to be the most convenient device for holding these pads during filtrations.

### Procedures

The coagulation tests involved bringing together the various amounts of kraft effluent, sea water or salt solution, and distilled water, mixing these ingredients by stirring for a selected time and determining the amount of material coagulated and any reduction of carbon caused by removing this material. Prefiltering of the kraft effluent and sea water prior to including these ingredients in mixtures was done in most cases and the media used is noted on curve sheets resulting from individual tests.

The amount of material coagulated was generally measured as follows:

1. Five hundred milliliters of coagulated mixture were filtered through a Watman Grade GF/C glass fiber filter pad.
2. The mixing vessel was rinsed and the retained material washed several times with distilled water.

3. The filter pad and retained material were dried at  $103^{\circ}\text{C}$  for at least two hours.
4. The filter pads and retained material were cooled in a dessicator.
5. The filter pads and retained material were weighed.
6. The amount of coagulated material was calculated as the difference between the weight of the filter pad plus retained material and the previously determined constant weight of the pad.

Volatility of the retained material was determined by repeating Step 3 at  $538^{\circ}\text{C}$ , followed by Steps 4 and 5. Percent volatility was calculated as the ratio of weight lost to initial weight.

Reductions in carbon associated with removal of coagulated material were determined by measuring the total and organic carbon content of filtrates from mixtures representing several different values of the independent variables.

Coagulated material was examined for chemical properties as follows:

1. Lignin content - digestion in concentrated sulphuric acid and volatility.
2. Nitrogen - digestion and distillation, as prescribed for the Kjeldahl procedure in Standard Methods, followed by nesslerization.

3. Sodium - flaming and reaction to a solution of zinc uranyl acetate as prescribed by Feigl (1953).
4. Magnesium - reaction to an alkaline solution of p-nitrobenzeneazoresorcinol as prescribed by Feigl.
5. Carbonate or bicarbonate - reaction to mineral acid.
6. Solubility - dissolution in several organic liquids.

### Results and Discussion

For presentation and discussion of results, quantitative tests are grouped into six experiments.

Experiment 1 - Coagulation versus time

Experiment 2 - Coagulation versus salinity from sea water

Experiment 3 - Coagulation versus kraft effluent concentration

Experiment 4 - Coagulation versus salinity from salt solutions

Experiment 5 - Reduction of effluent suspended matter due to coagulation by sea water

Experiment 6 - Coagulation versus pH

Experiment 1. Figure 2 graphically shows the results of the first tests included in Experiment 1. These tests represent the only exception to the general procedure described previously for measuring coagulated material. In this case glass wool was used to prefilter the kraft effluent and sea water before combining these ingredients. Filtering of coagulated mixtures was done with Gooch crucibles holding 2.0 cm diameter filter pads. From 50 to 80 milliliters of mixture could be filtered in this manner but subsequent washing of the retained material was not possible because of clogging of the filter pads.

These tests indicate that essentially all coagulation took place within 30 minutes after combining ingredients. A decrease in the amount of material coagulated during separate tests parallels aging of the kraft effluent. Several days elapsed between the individual tests and during this time adsorption of some of the fine material onto fibers and larger particles probably occurred. This resulted in increasing amounts of material being retained during prefiltering of ingredients. A corresponding increase in volatility of coagulated material took place along with the aging of kraft effluent. Seven-day effluent resulted in coagulated material which was from 50% to 60% volatile. Volatility increased to about 90% as aging progressed to 3 weeks. No change in total alkalinity and pH of mixtures

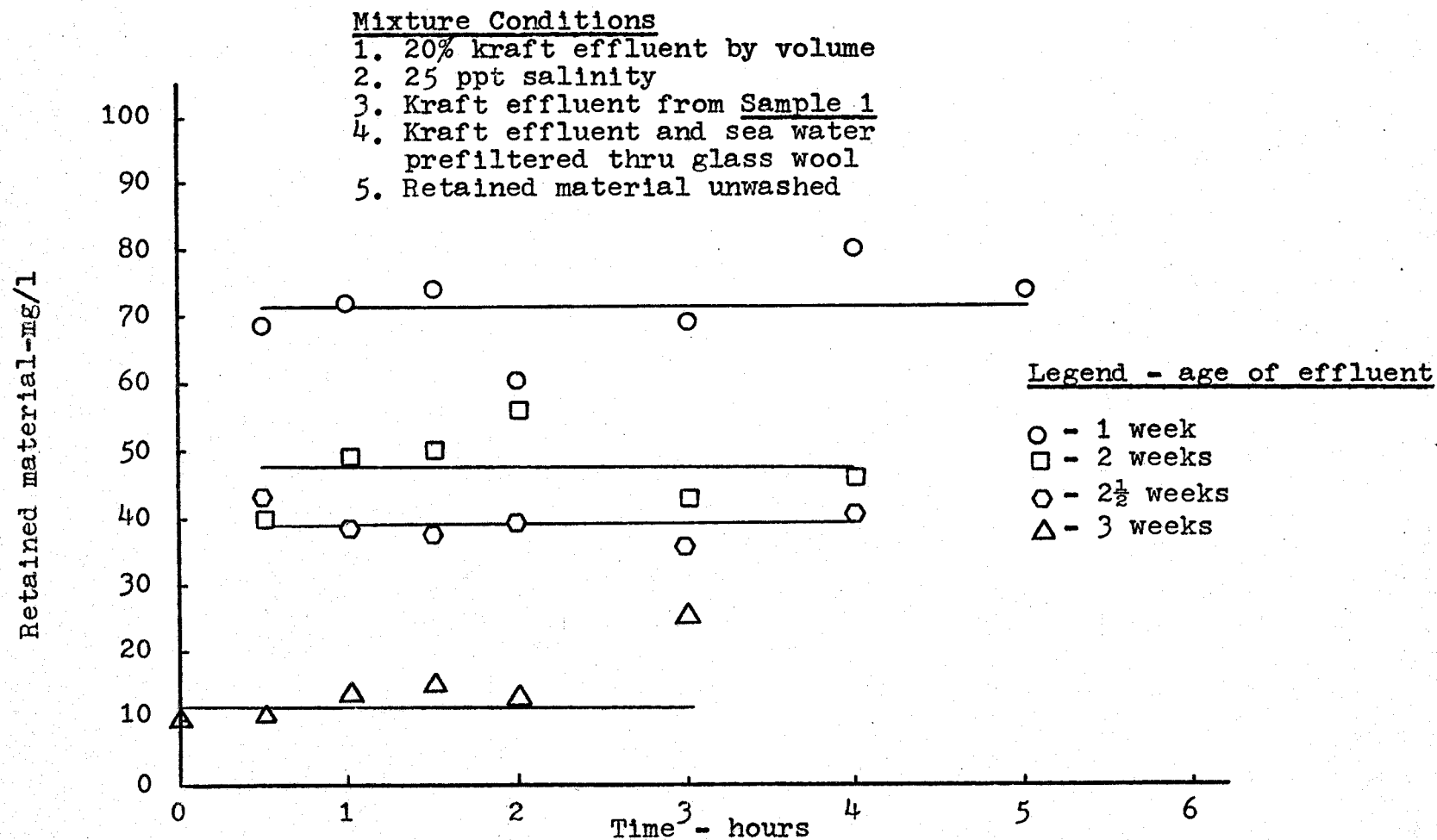


Figure 2. Retained material versus time

and filtrates was observed during these tests.

The carbon content of filtrates from mixtures containing the 3-week old effluent is shown in Figure 3. These results substantiate those represented in Figure 2 by showing that most of the decrease in total carbon occurred within 30 minutes after combining ingredients. A secondary decrease in organic carbon occurred after the first hour and corresponded to an increase in inorganic carbon. Absorption of carbon dioxide by the alkaline mixtures could have resulted in the precipitation of carbonate or bicarbonate onto which a small amount of carbonaceous material may have adsorbed and caused the small secondary decrease in organic carbon. The coagulation due to sea water probably caused the effects occurring in the first 30 minutes.

Results of other tests within Experiment 1 are plotted in Figures 4 and 5. The general procedure outlined previously for measuring coagulated material was followed in these and all subsequent tests. Results shown in Figure 4 indicate that all coagulation was essentially complete within 30 minutes after combining ingredients. The material separated was found to be 100% volatile.

Results plotted in Figure 5 also show coagulation to be essentially complete within 30 minutes. Very little of the fine material was coagulated from mixtures with filtered ingredients. Nearly all of the 17 mg/l which was separated

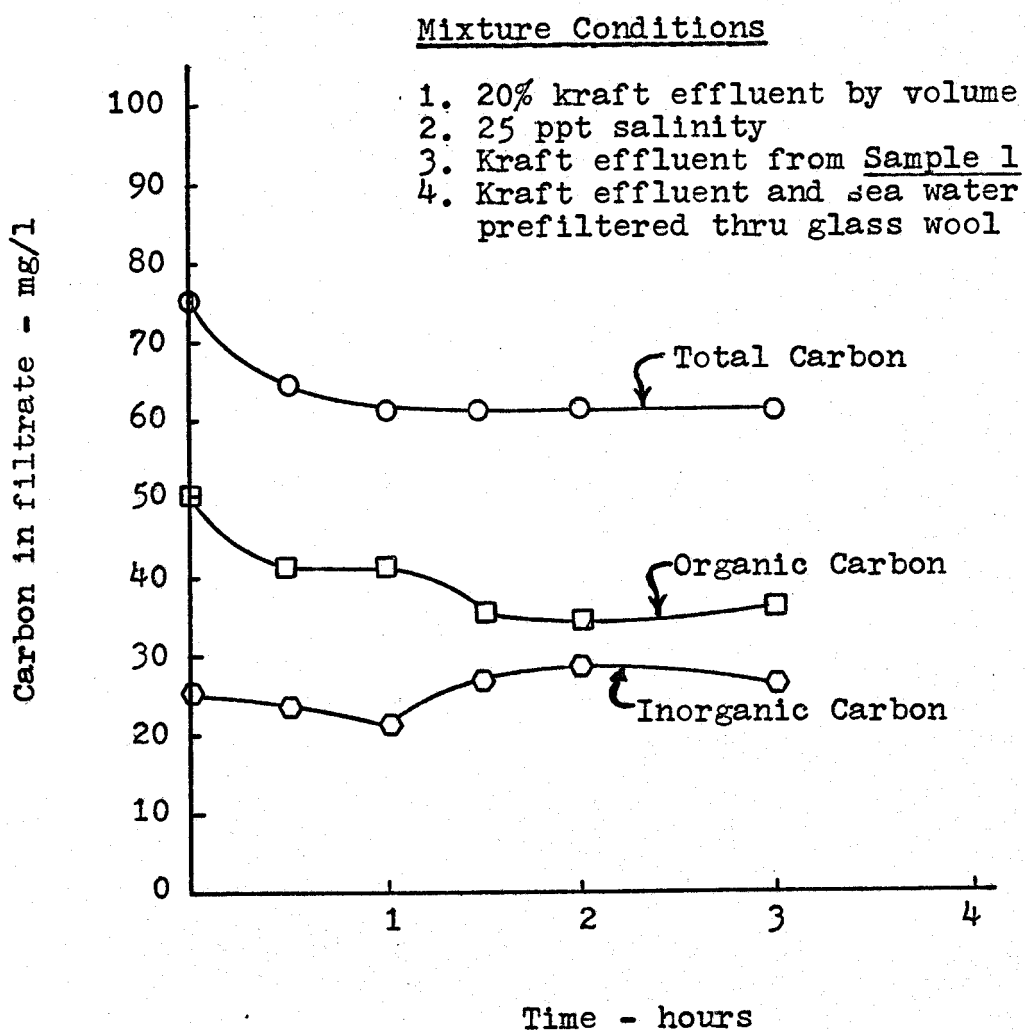


Figure 3. Filtrate carbon versus time

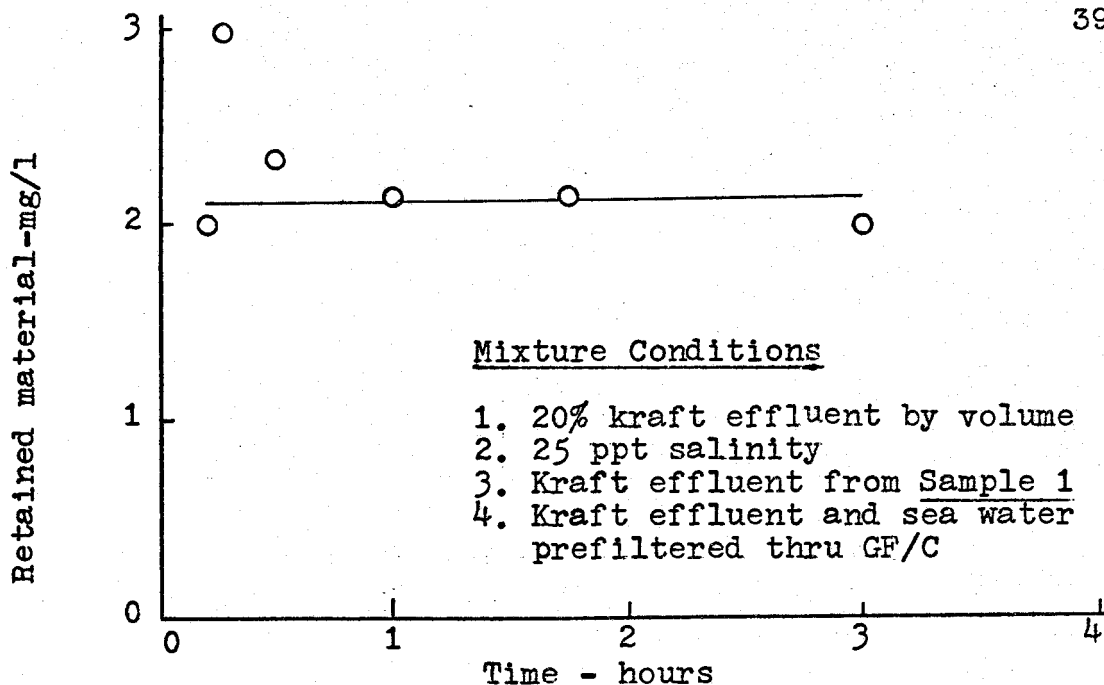


Figure 4. Retained material versus time

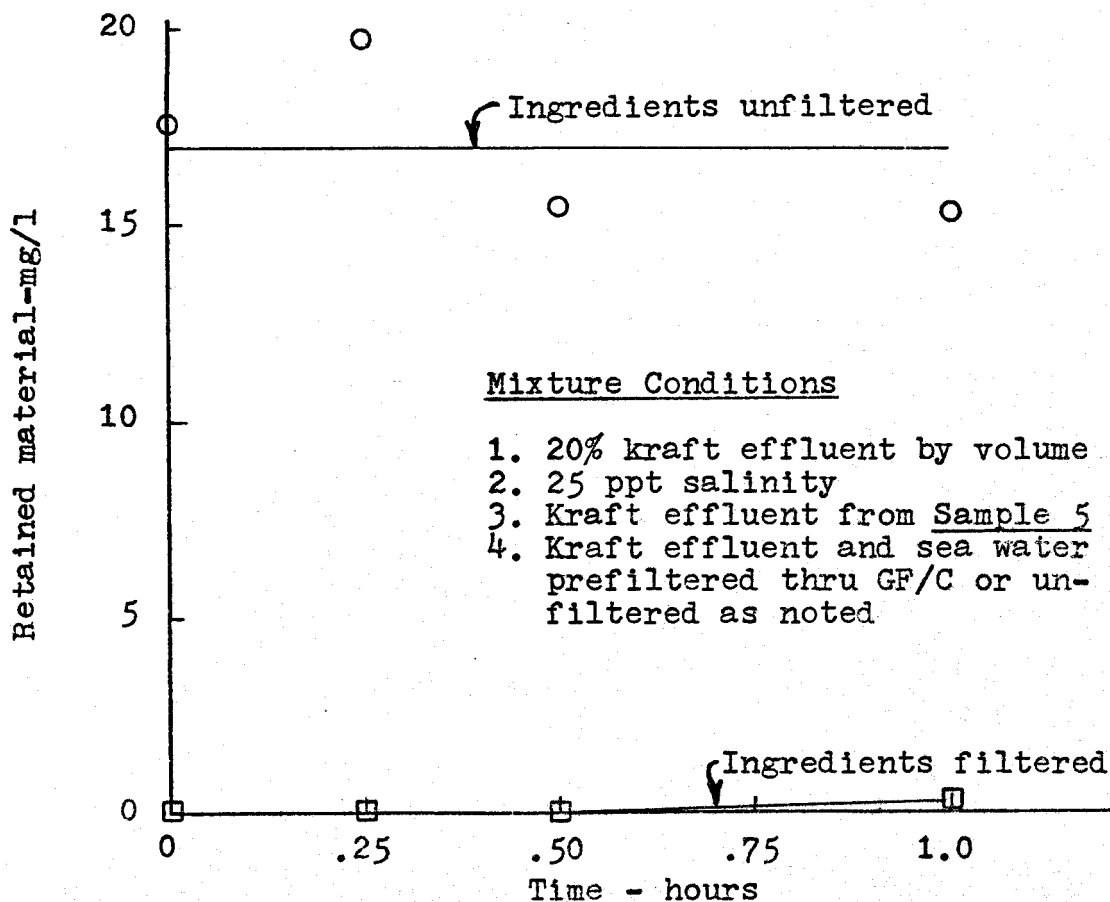


Figure 5. Retained material versus time



from the mixtures with unfiltered ingredients was due to suspended solids initially present. Material separated from mixtures with filtered ingredients was 100% volatile and the material separated from mixtures with unfiltered ingredients was 77% volatile. The results of these tests suggest that readily detectable coagulation by sea water does not occur with all kraft effluents.

Based upon the results of Experiment 1, 30 minutes was adopted as the standard stirring time for mixtures in all subsequent tests.

Experiment 2. The effect of salinity of sea water upon coagulation in kraft effluent was evaluated in Experiment 2 and the results are shown in Figures 6 through 10. A general increase in coagulation with salinity is indicated for the four effluent samples tested.

The variation in observed data from this experiment is probably due to random errors which may amount to a significant percentage of the small amounts of material involved. A considerable difference was observed in the amounts of material coagulated in the various samples of kraft effluent. About twice as much material was coagulated in Sample 3 as in Sample 2, whereas Sample 4 produced no coagulation and Sample 5 an indefinite amount. A significant point about the results of Experiment 2 is the small amount of material coagulated in all samples.

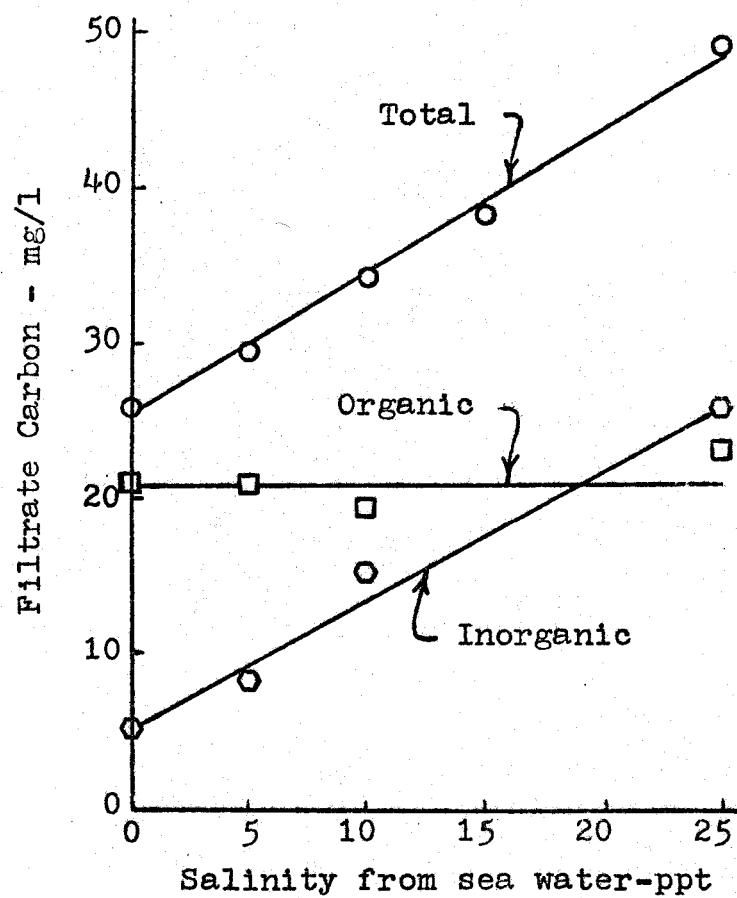
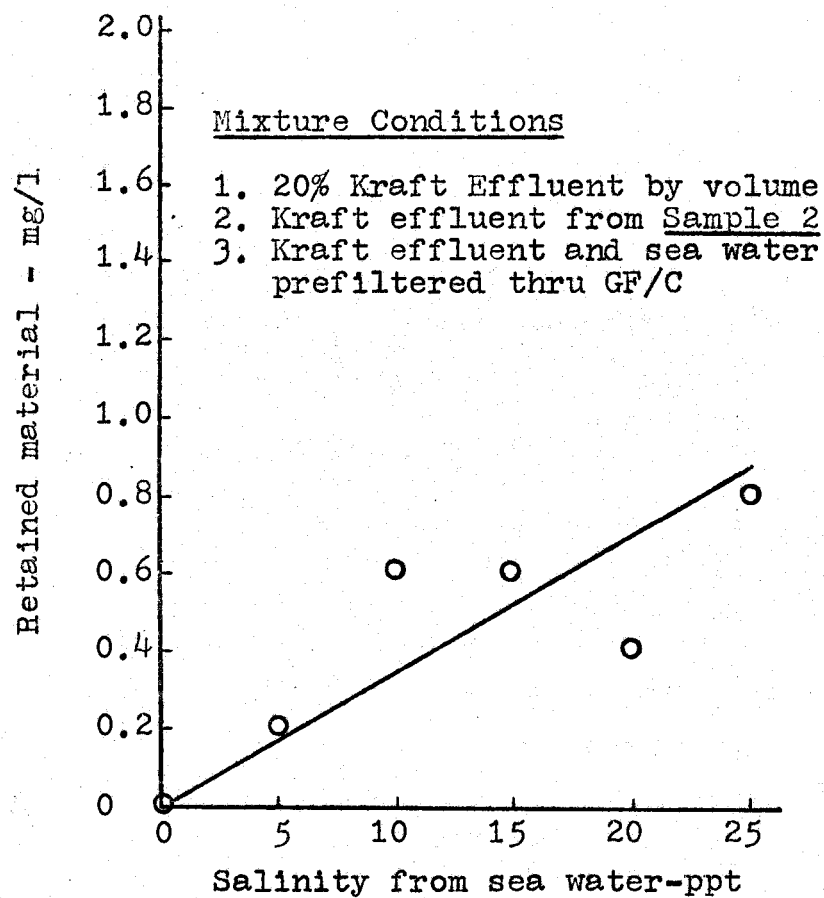


Figure 6. Retained material and Filtrate carbon versus Salinity from sea water

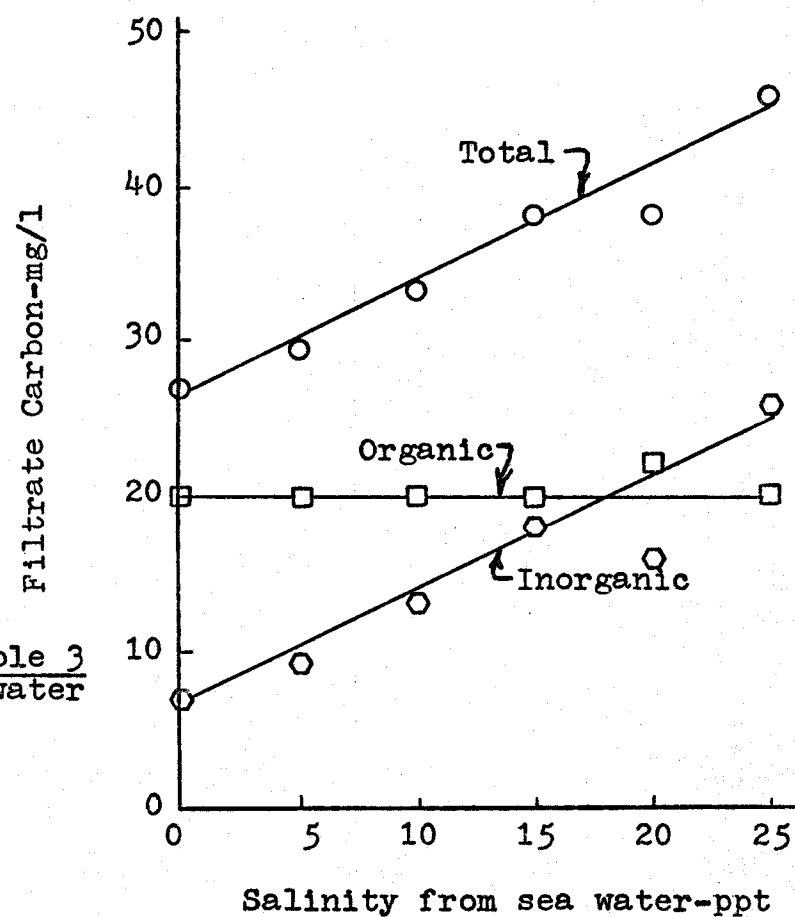
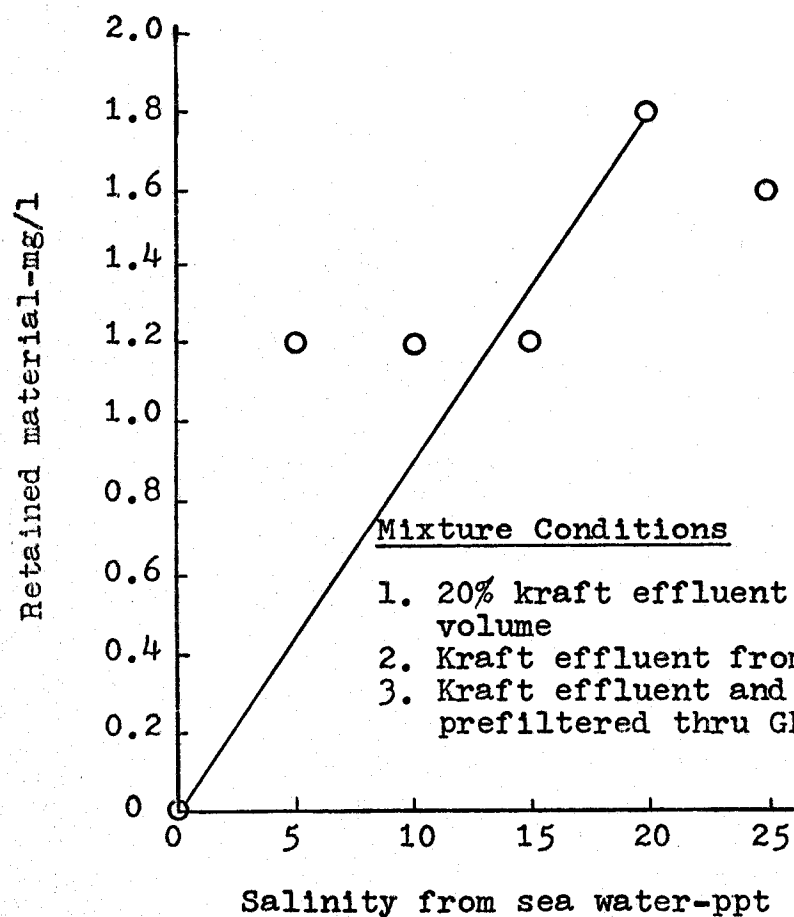


Figure 7. Retained material and Filtrate carbon versus Salinity from sea water

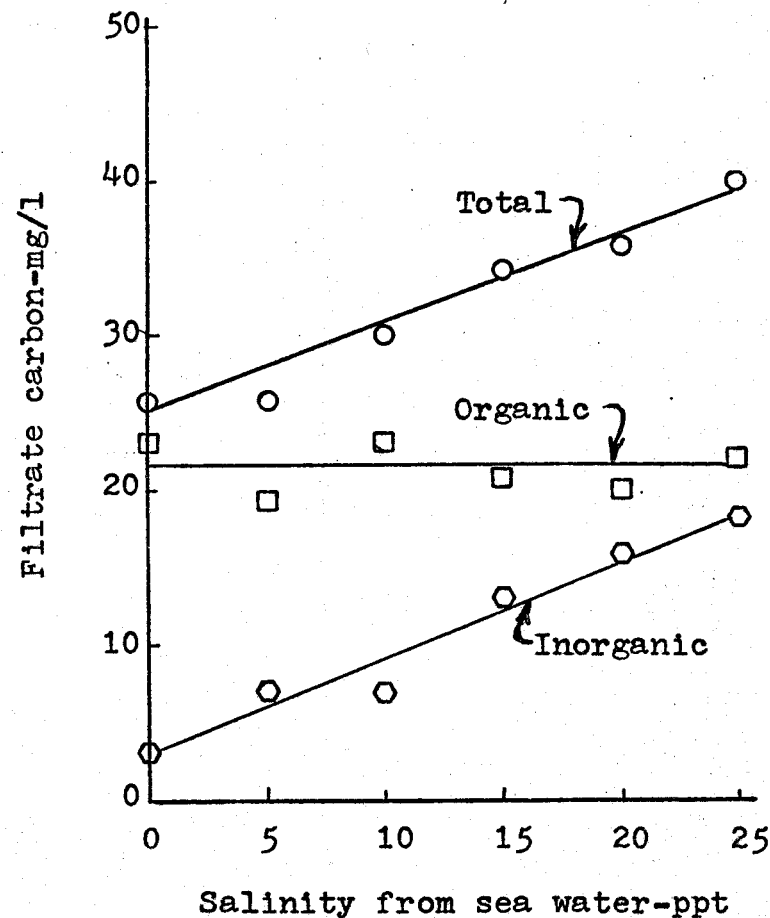
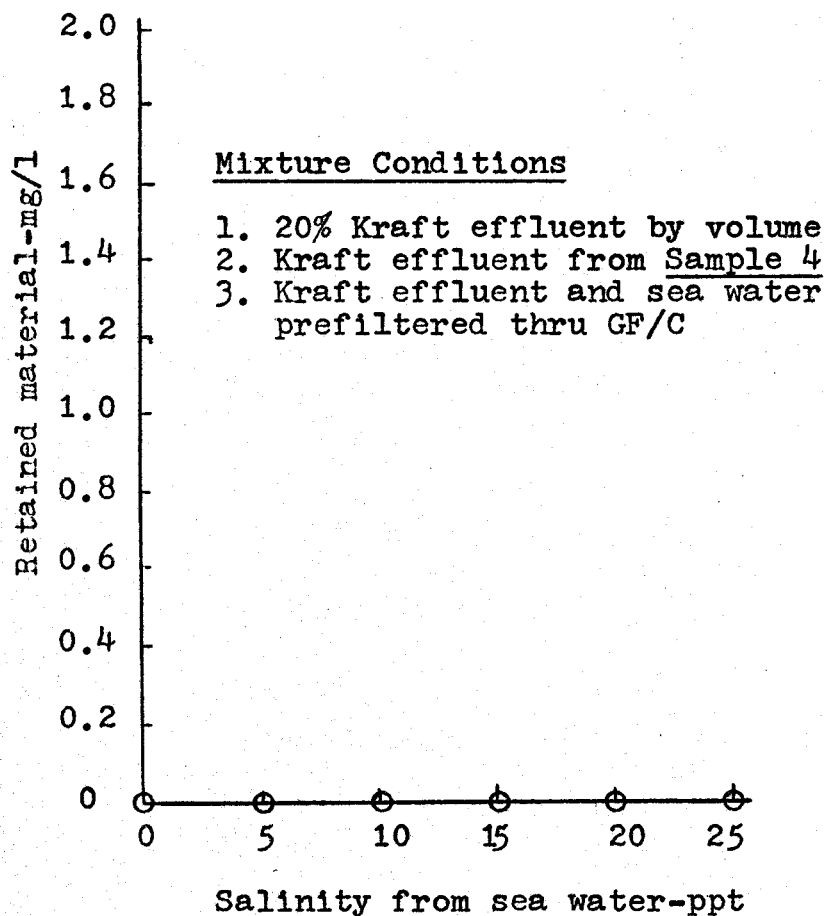


Figure 8. Retained material and Filtrate carbon versus Salinity from sea water

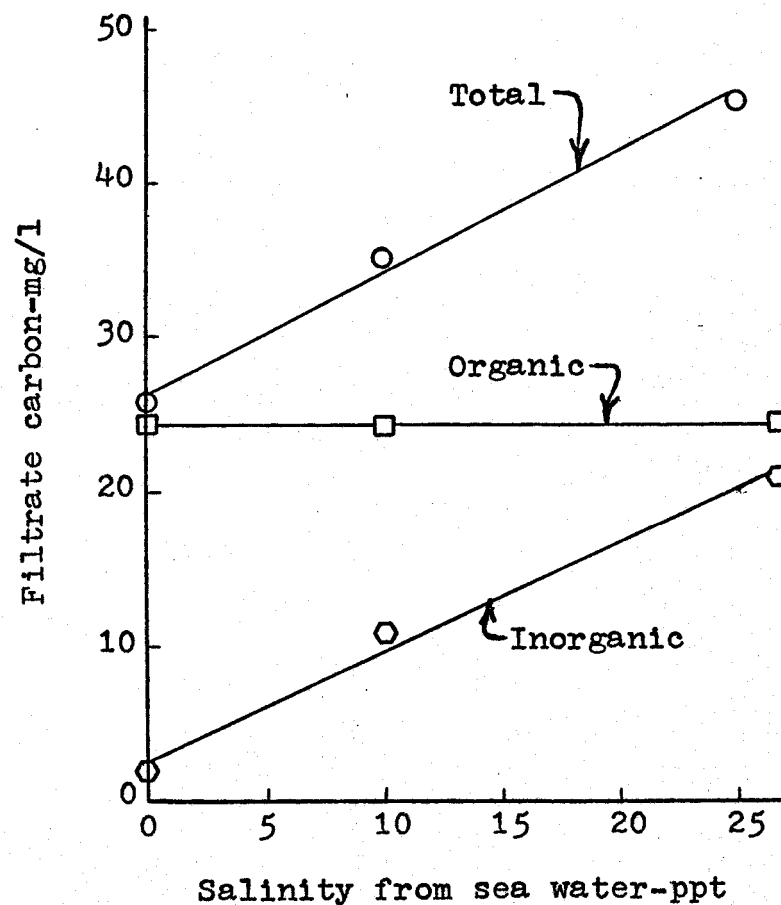
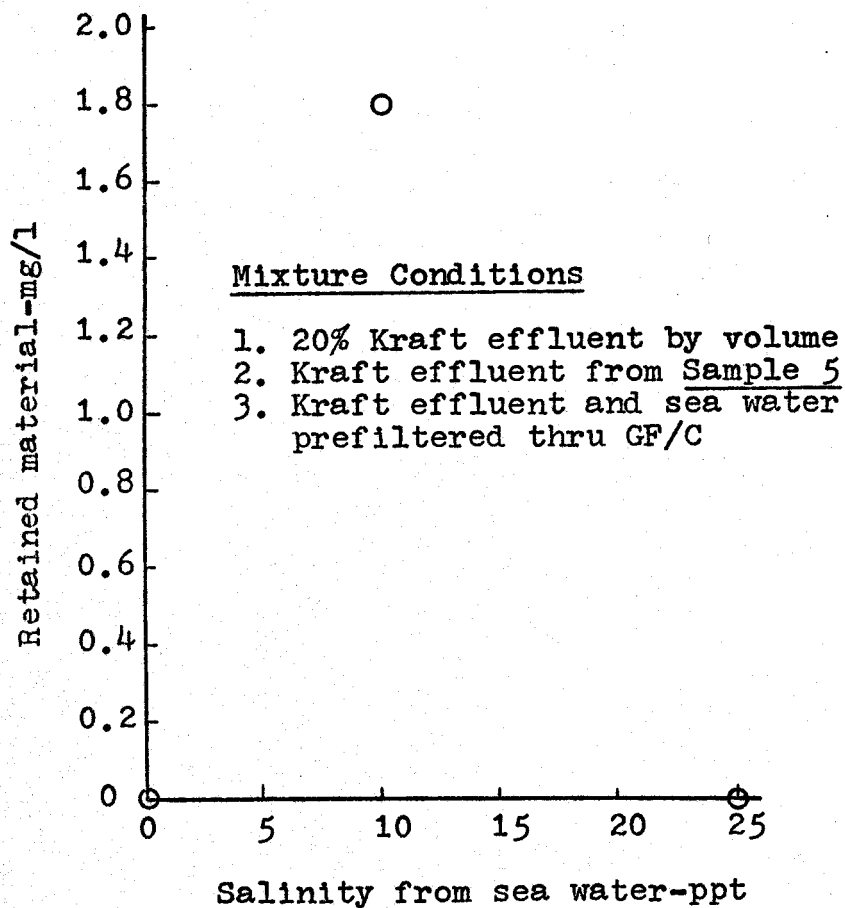


Figure 9. Retained material and Filtrate carbon versus Salinity from sea water

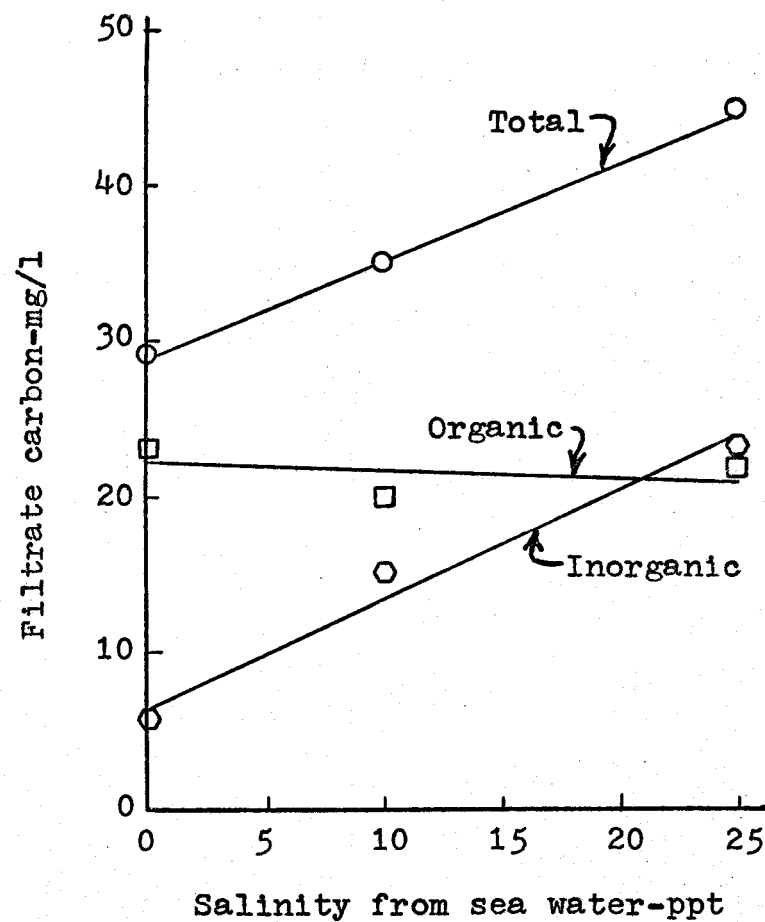
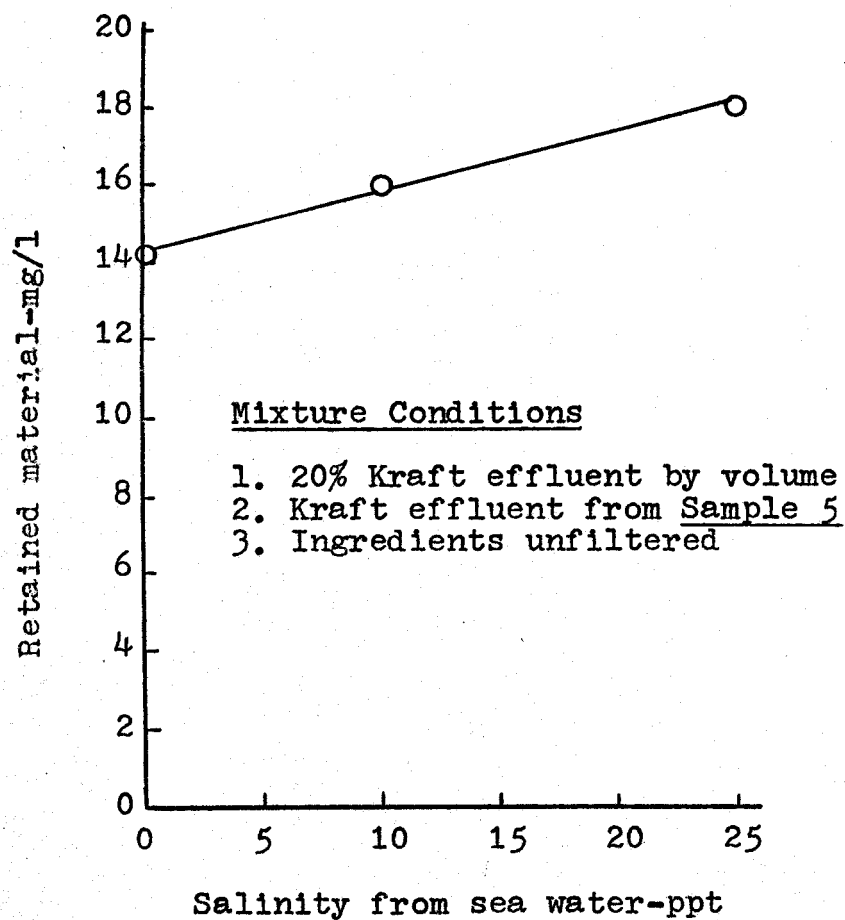


Figure 10. Retained material and Filtrate carbon versus Salinity from sea water

No significant removal of carbon with coagulated material is indicated by the tests in Experiment 2. This is shown by the constant amount of organic carbon present, at all salinities. The increase in total carbon is due to added amounts of inorganic carbon from sea water as salinity is increased.

Figures 6 through 9 represent results of tests with mixtures of prefiltered ingredients. The variation in coagulation with salinity which occurred in mixtures of unfiltered ingredients is shown in Figure 10. The 14.2mg/l of retained material at zero salinity is slightly below the amount expected from suspended solids initially present in the kraft effluent. This is probably due to the aging of the effluent. About 4 mg/l of material was retained due to coagulation by sea water. A small removal of organic carbon as a result of coagulation is indicated. The amount of inorganic carbon is somewhat greater than in mixtures with filtered ingredients which indicates that some of this type of material is removed during prefiltering of ingredients.

Experiment 3. The variation in amounts of material coagulated with changes in kraft effluent concentration was evaluated in Experiment 3. Results are shown in Figures 11 through 16. An increase of coagulated material with effluent concentration is indicated by all tests. As shown

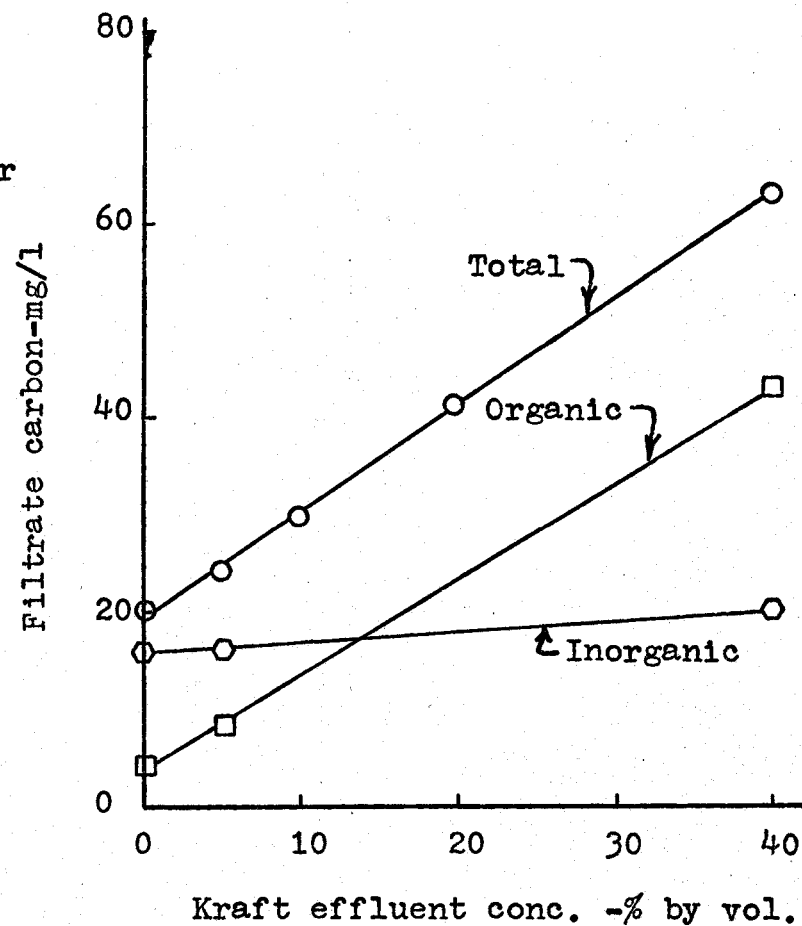
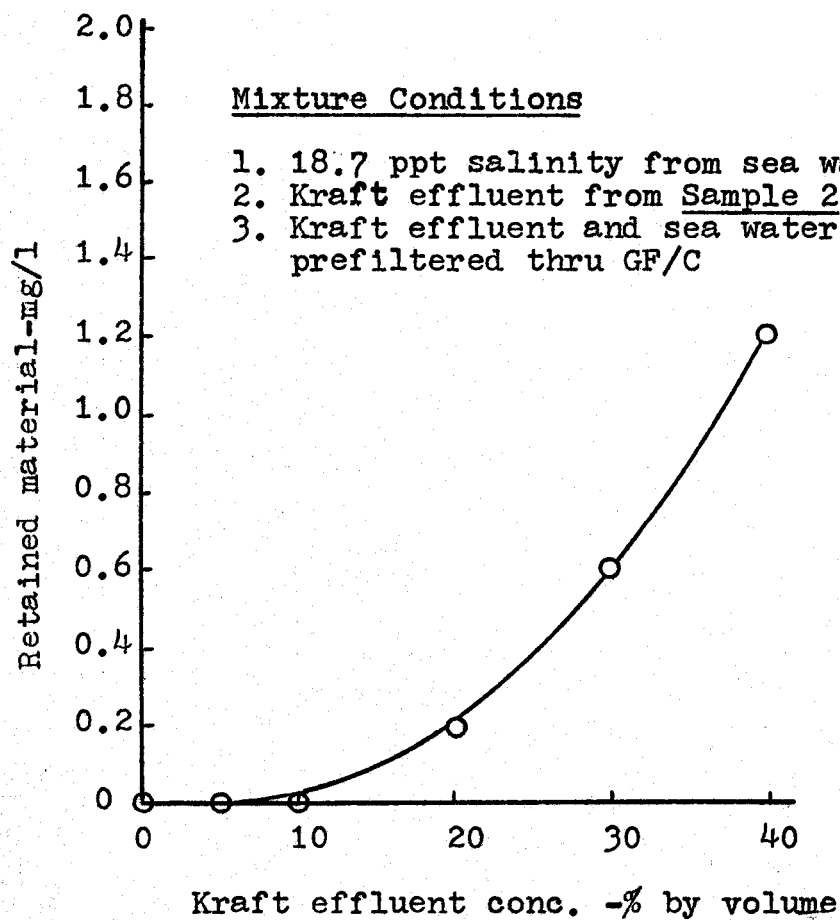


Figure 11. Retained material and Filtrate carbon versus Kraft effluent concentration



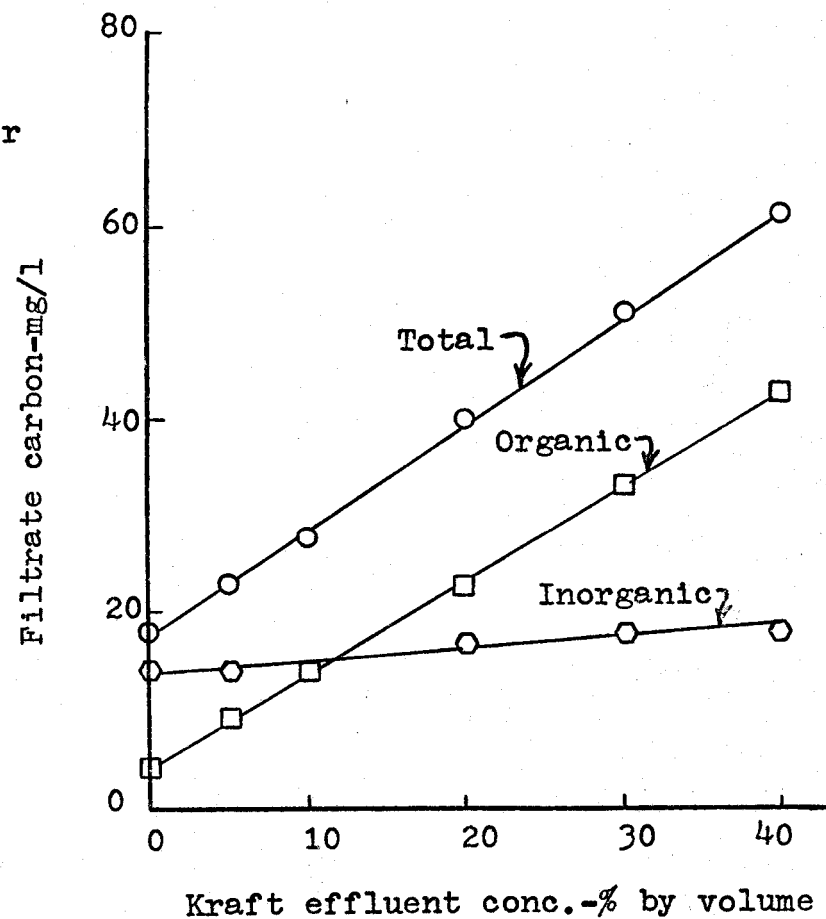
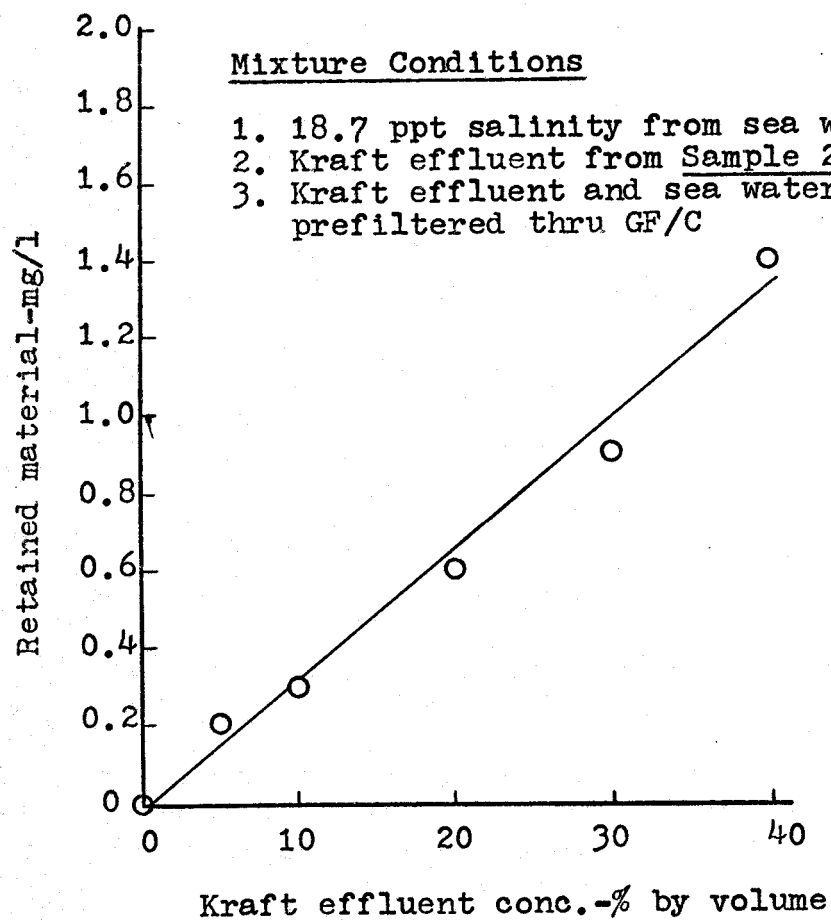


Figure 12. Retained material and Filtrate carbon versus Kraft effluent concentration

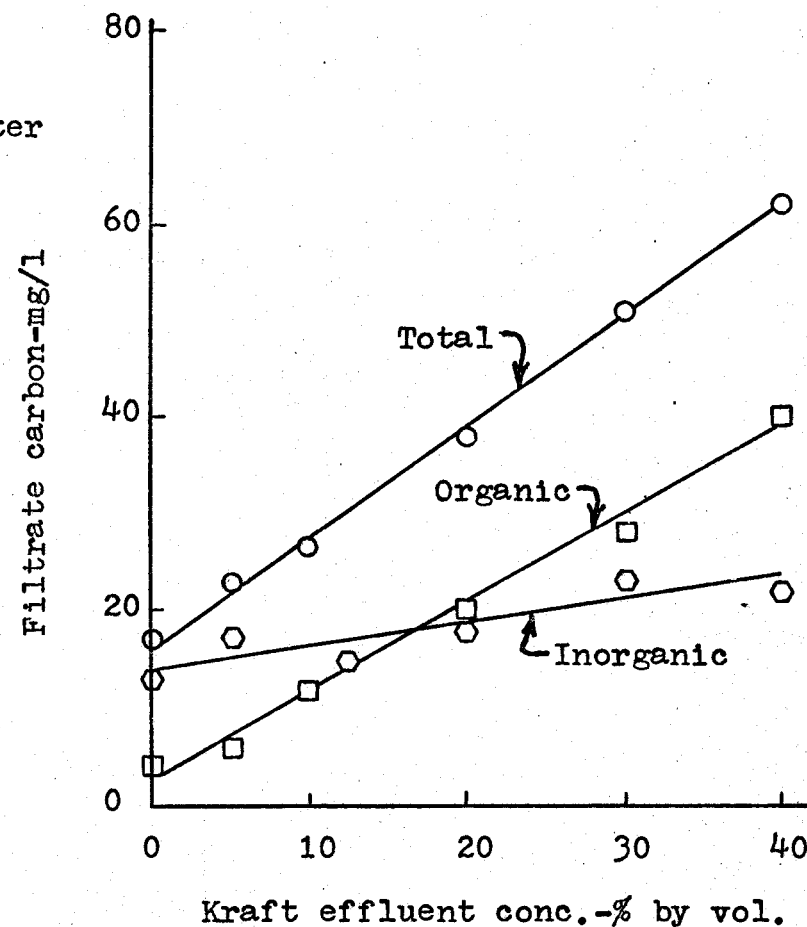
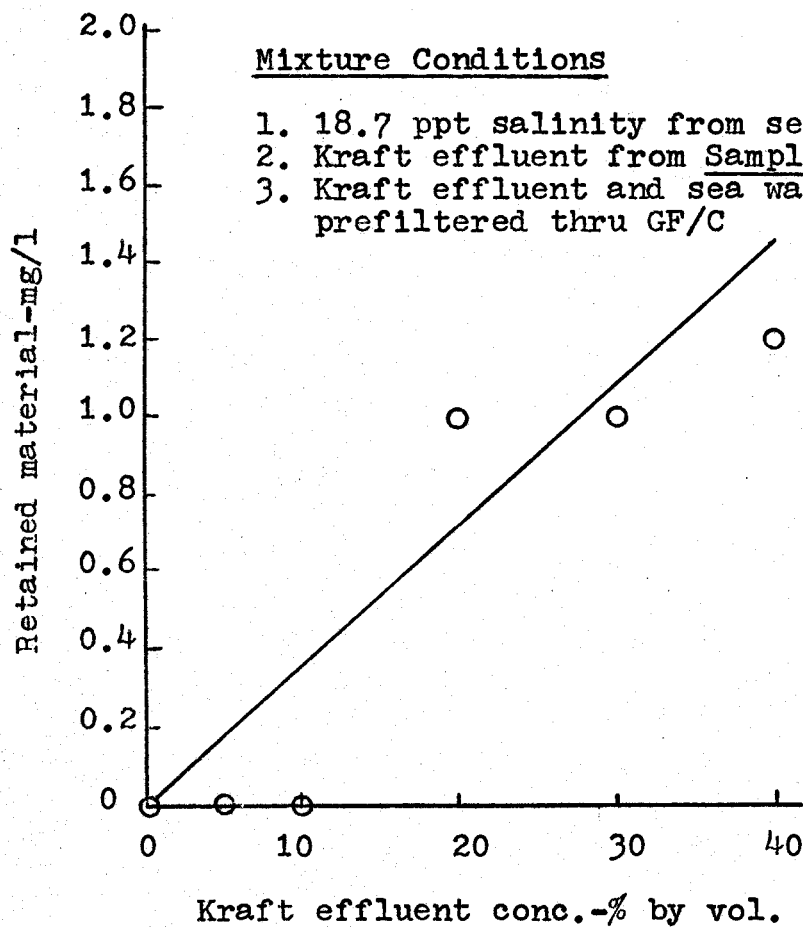


Figure 13. Retained material and Filtrate carbon versus Kraft effluent concentration

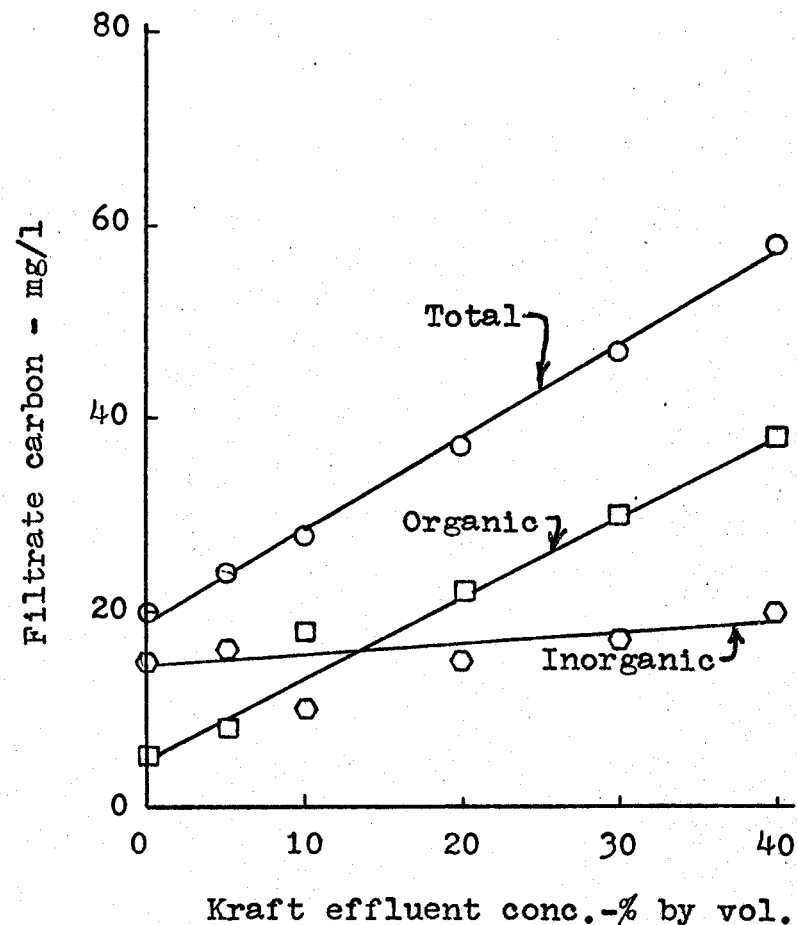
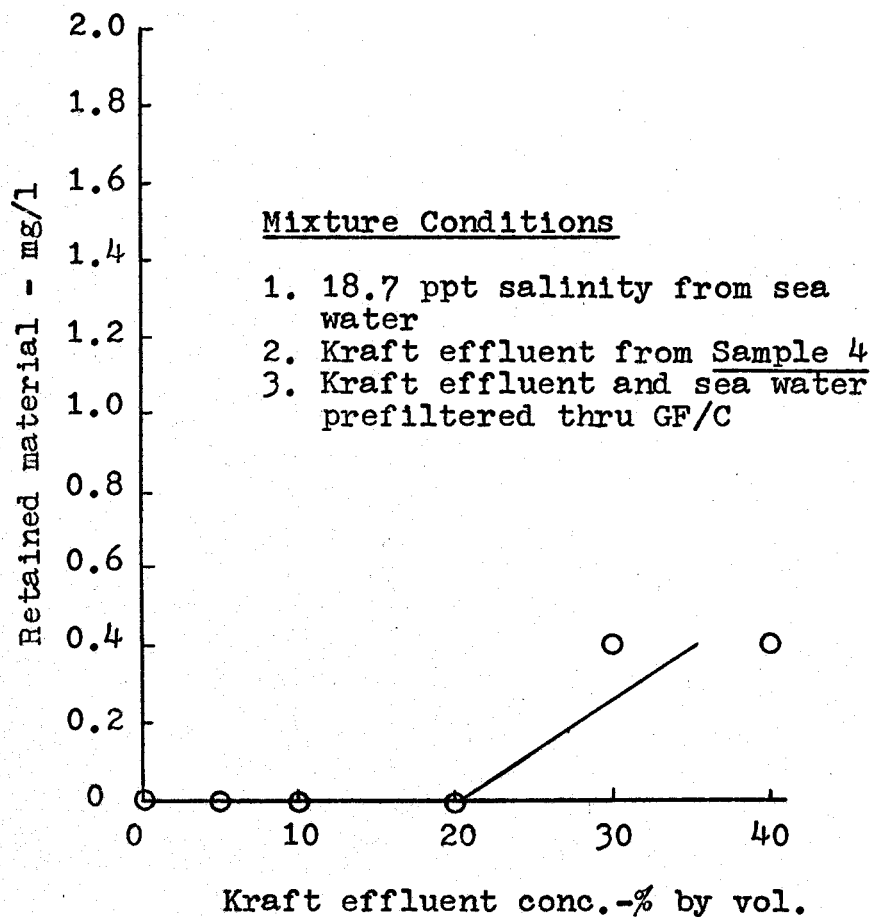


Figure 14. Retained material and Filtrate carbon versus Kraft effluent concentration

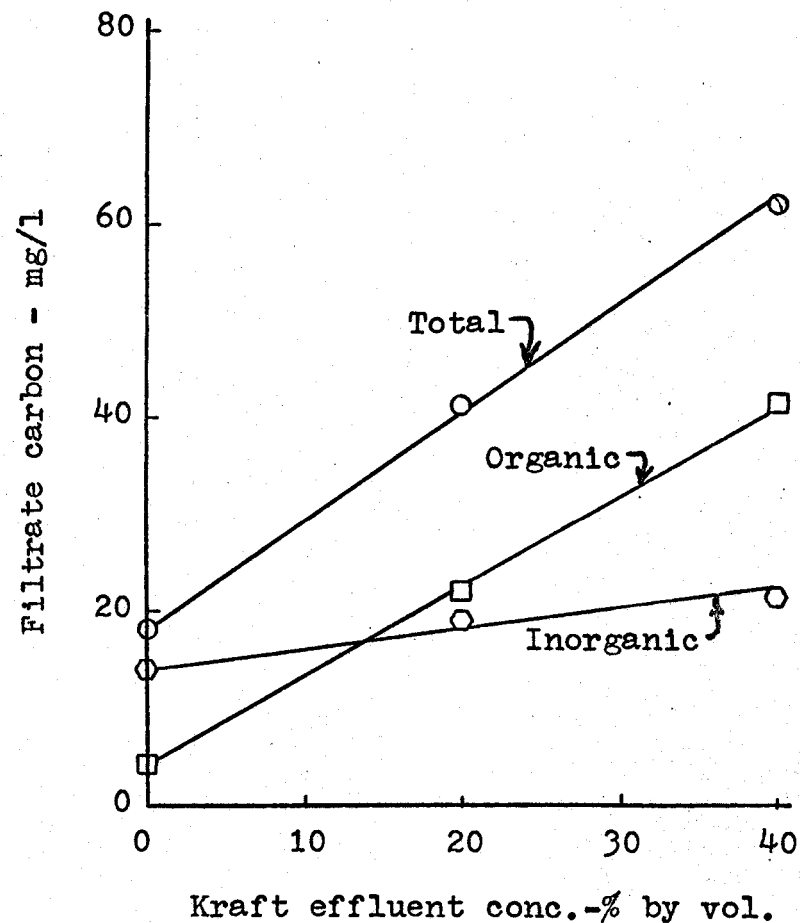
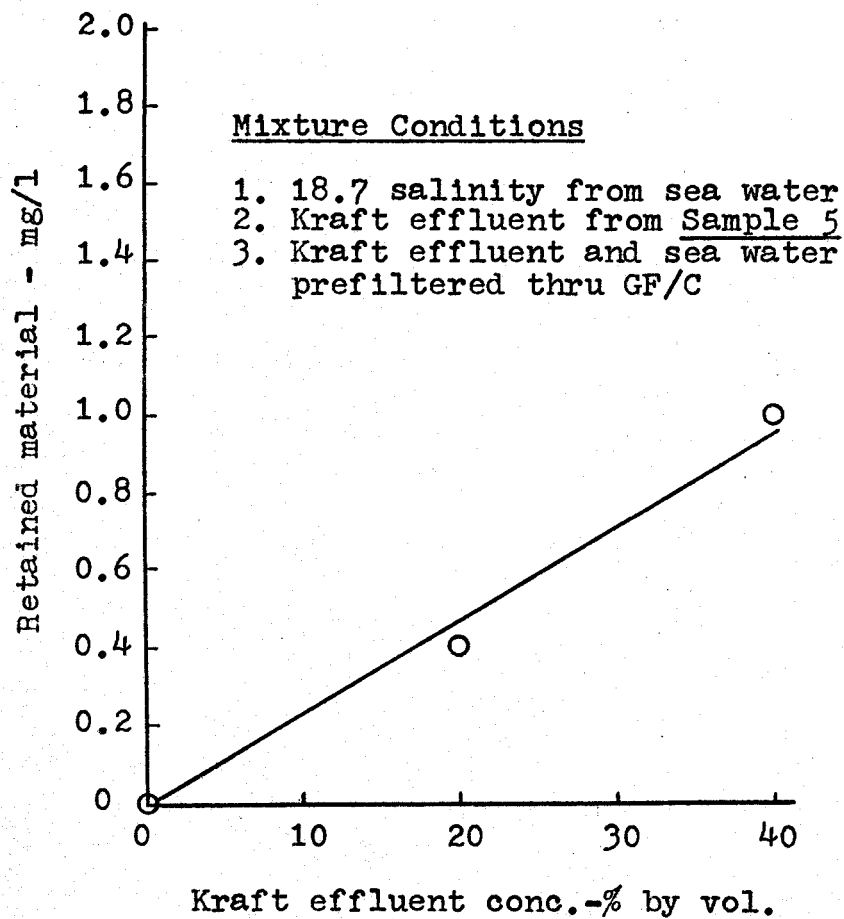


Figure 15. Retained material and Filtrate carbon versus Kraft effluent concentration

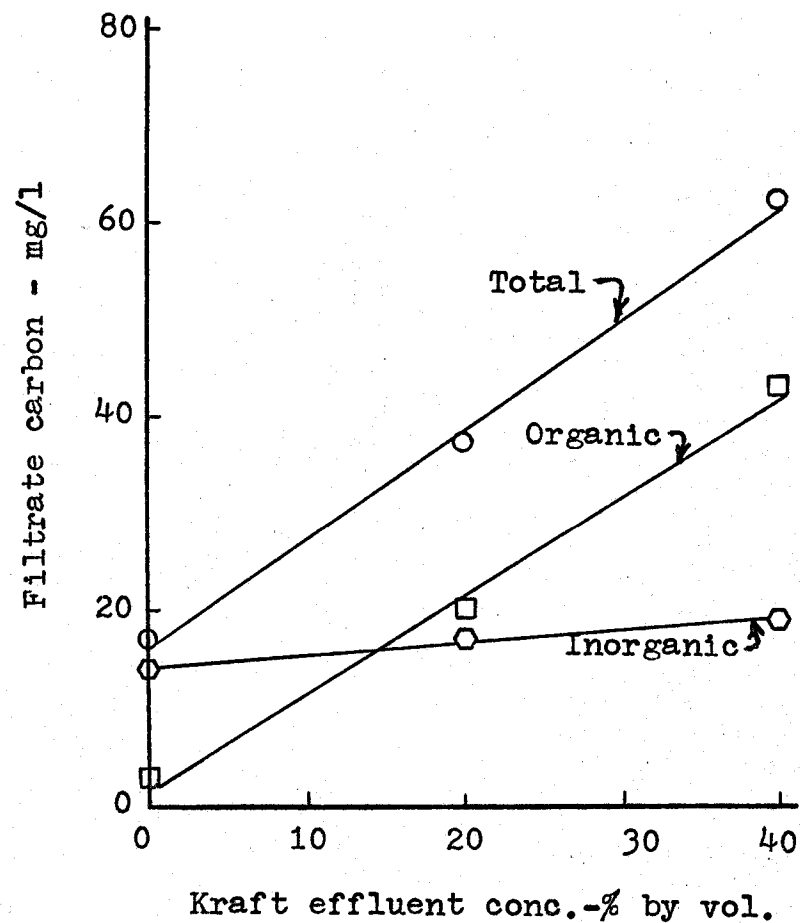
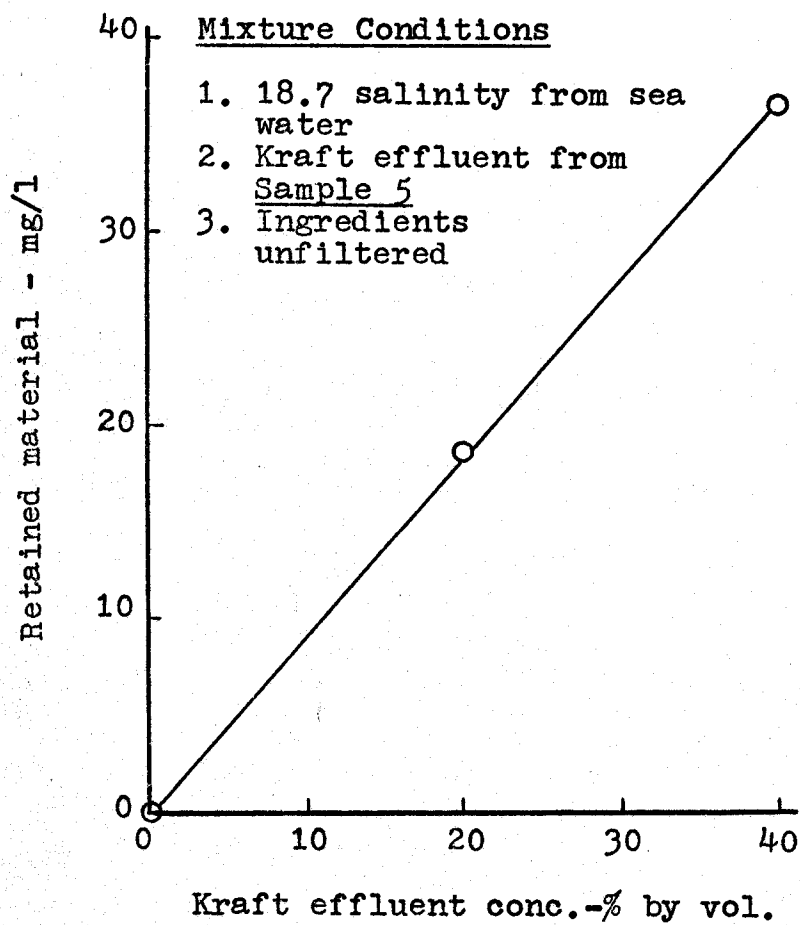


Figure 16. Retained material and Filtrate carbon versus Kraft effluent concentration

in Figures 11 and 12 there was a variation between different tests with the same effluent sample. This was probably due to random errors which may have amounted to a considerable percentage of the small amounts of material measured. No coagulation occurred in mixtures containing effluent from Sample 4 at effluent concentrations below 20%. This finding agrees with results obtained in Experiment 2 and shown in Figure 8. The material coagulated in mixtures with pre-filtered ingredients was about 65% volatile and that from mixtures with unfiltered ingredients was about 80% volatile. As was the case in Experiment 2, the most significant observation from the tests of Experiment 3 is the small amount of material coagulated in all mixtures.

Experiment 4. Solutions of salts containing some of the most abundant elements in sea water were used as coagulants in Experiment 4. The results are shown in Figures 17, 18 and 19. In order to accent their effect, the ion concentrations in these solutions were much higher than the levels occurring in sea water.

The voluminous amount of material separated from kraft effluent by the sodium chloride solution is reflected in Figure 17. When dried, this material consisted of a combination of clear crystal, white powder and a light tan colored substance. These components dried into a conglomerate solid in which each component was well defined from

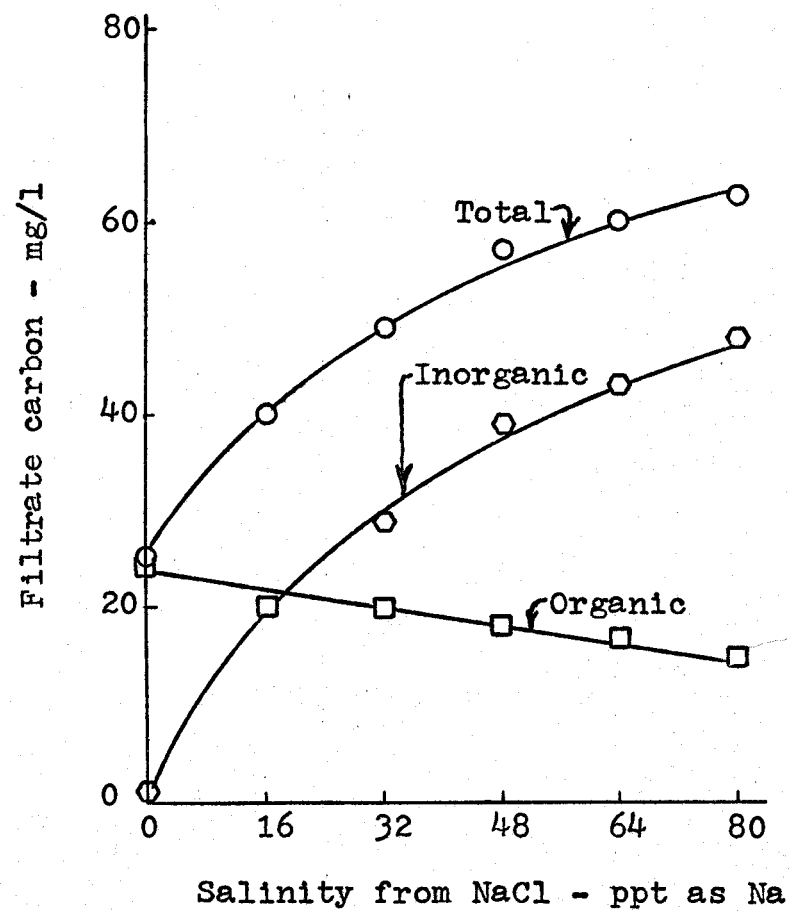
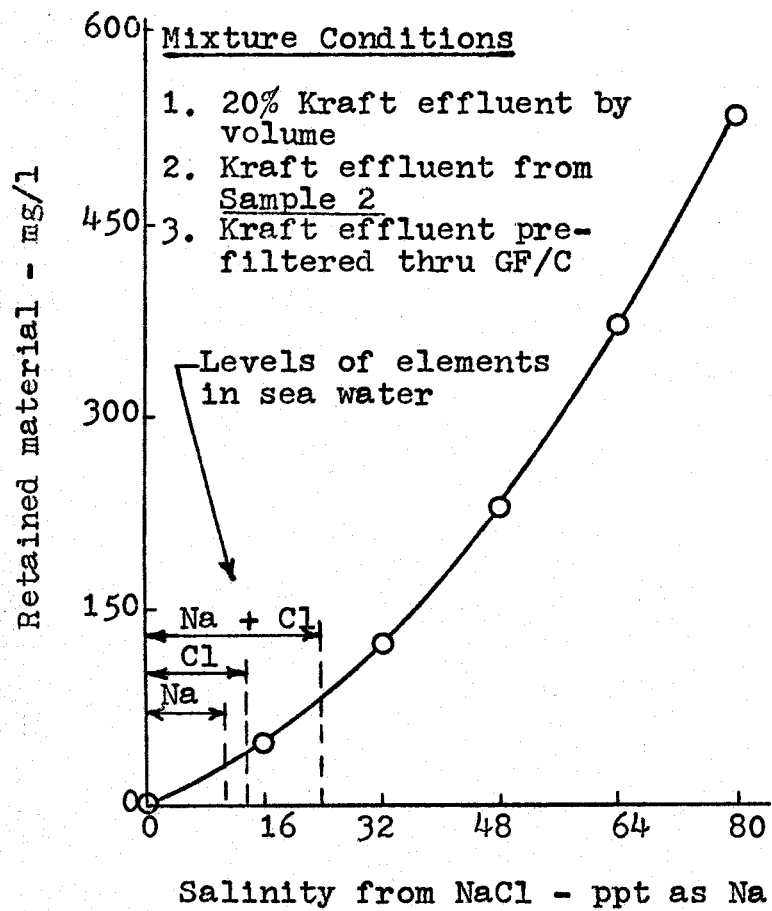


Figure 17. Retained material and Filtrate carbon versus Salinity from Sodium chloride solution

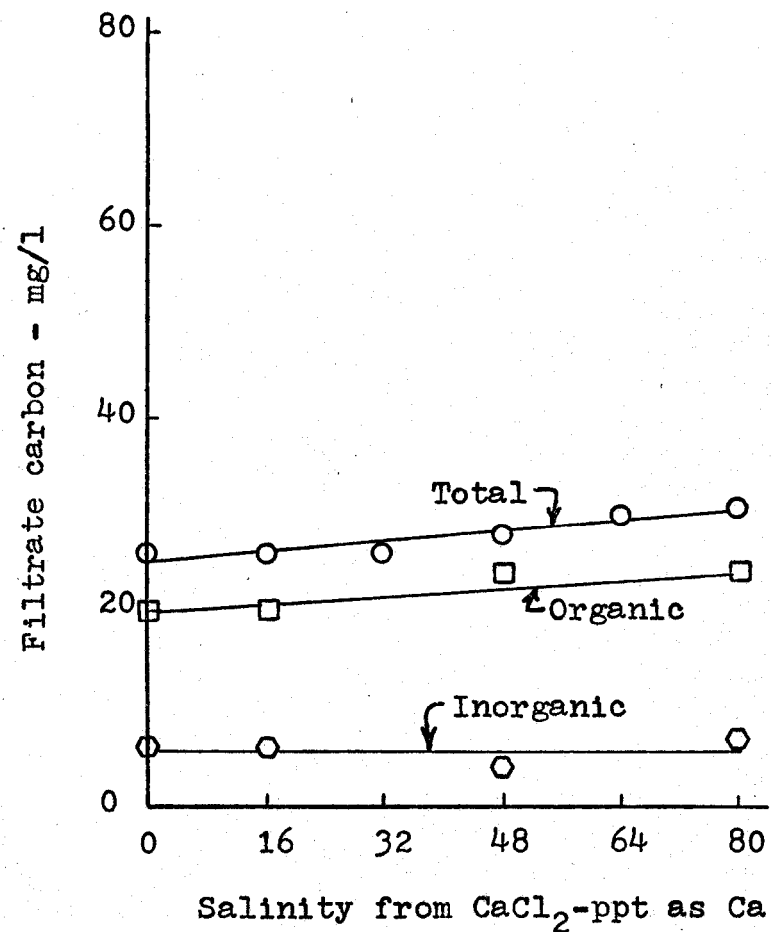
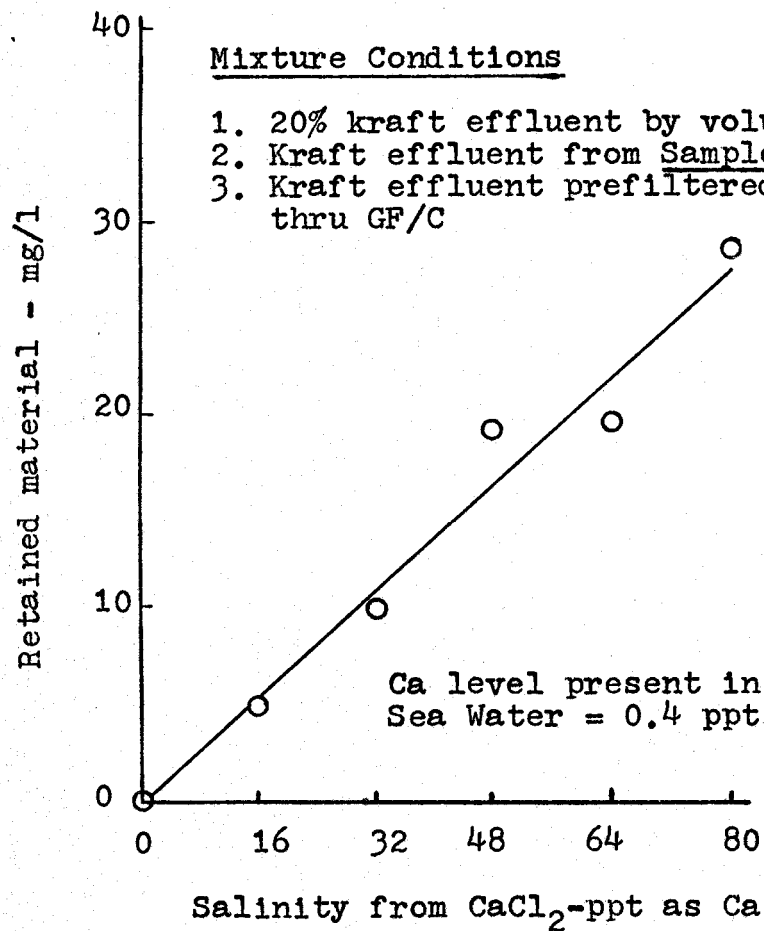


Figure 18. Retained material and Filtrate carbon versus Salinity from Calcium chloride solution



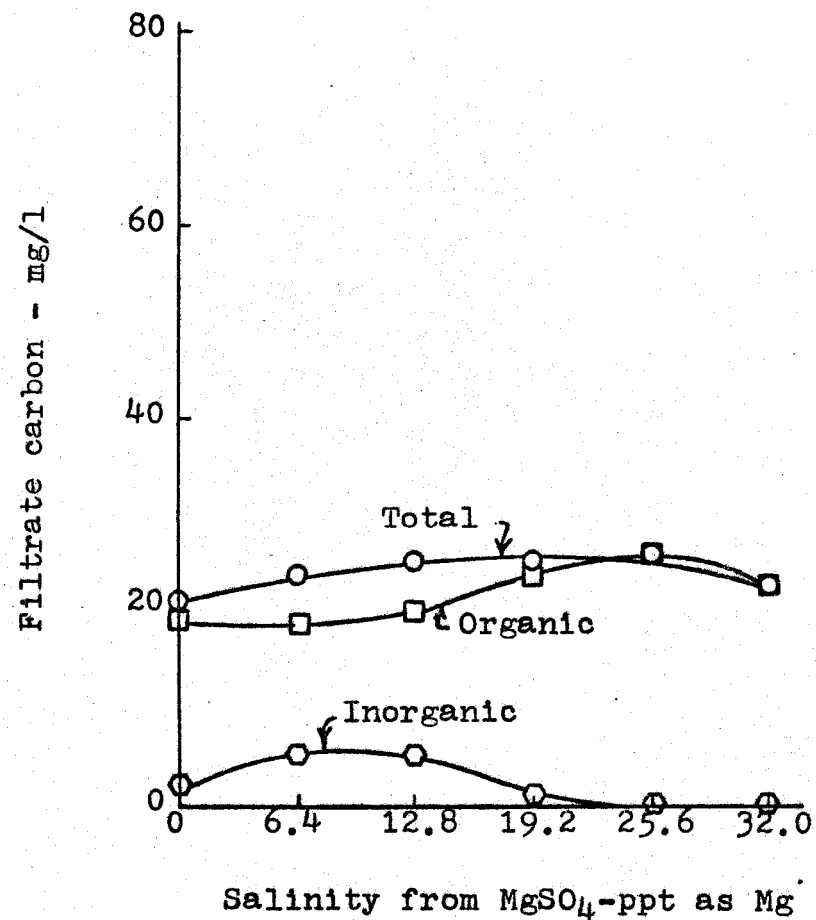
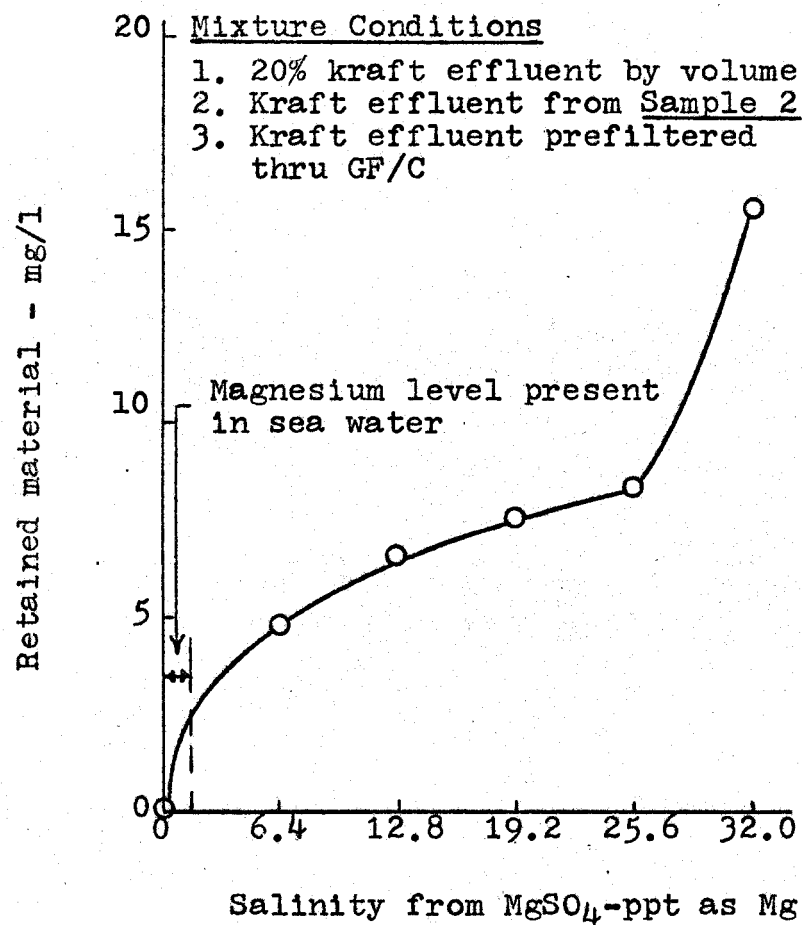


Figure 19. Retained material and Filtrate carbon versus Salinity from magnesium sulfate solution

the other two. The conglomerate material was approximately 50% volatile. The clear crystalline material was probably sodium chloride and the white powder was possibly sodium carbonate or bicarbonate. The tan substance was an acid insoluble material which appeared to be very similar to that coagulated by sea water. An abundance of sodium present in the coagulated material was detected by flaming and by the quantity of sodium zinc uranyl acetate precipitated when zinc uranyl acetate solution was added to a suspension of the coagulated material. Identification of carbonate or bicarbonate was based upon the evolution of gas which occurred when mineral acid was added to the dried conglomerate.

Separation of material designated by that portion of the curve with an increasing slope was probably due to several factors, including the formation of insoluble compounds onto which colloidal organic material was adsorbed or an adjustment of zeta potentials which resulted in coalescence and precipitation of colloidal organic material. The presence of three distinct components in the separated material suggests that more than one mechanism was involved. As the level of salinity increased a salting out process probably became significant as indicated by the nearly constant slope.

When compared to equivalent levels in sea water it is significant to note that in pure solution sodium and chloride ions are much more effective in causing coagulation of

kraft effluent. About 90 mg/l of material was coagulated from kraft effluent by these ions from pure sodium chloride solution, compared to less than 1 mg/l for an equivalent ionic concentration in sea water. The ions in sea water are possibly bound in some manner which prevents them from reacting effectively.

A nearly complete removal of color from the kraft effluent accompanied the coagulation by sodium chloride solution. Color was imparted to a sulphuric acid solution when some of the conglomerated material was placed in suspension. After digestion in the acid for two hours a great deal of black material appeared in suspension along with the disappearance of the amber color of the kraft effluent. Upon consultation with chemists involved in forest products research, it was concluded that the tan-colored material was probably an acid insoluble (Klason) lignin. When subjected to flame this material was volatile which also aided in characterizing it as a lignin.

A definite decrease in filtrate organic carbon occurred with the coagulation by sodium chloride solution. The removal of the tan colored material was probably the source of this decrease. The increase in inorganic carbon was evidently due to the presence of sodium carbonate or bicarbonate in the salt solution. A partial precipitation of the carbonate or bicarbonate with increasing salinity is

indicated by the decreasing slope of the inorganic carbon curve.

Calcium chloride solution was much less effective as a coagulant. Figure 18 indicates that only 10% as much material was coagulated by the calcium solution when compared to similar salinities from sodium chloride solution. If the coagulation was principally the result of an adjustment of zeta potential, the Schulze-Hardy rule would indicate that calcium ions should be from 20 to 80 times as effective as sodium ions in causing coagulation. Results did not reflect this greater effectiveness and therefore the separation of material was probably due principally to the precipitation of inorganic reaction products. The fact that no decrease in organic carbon was caused by the calcium chloride solutions supports this proposition. It also points out that the chloride ion is not effective in causing coagulation of kraft effluent. Kraft effluent has been characterized as a lyophilic sol in which the organic colloids are shielded by a layer of water. The greater solubility of sodium in water could enable this ion to be more effective than calcium, chloride, or magnesium ions in penetrating the protective shell of water and decreasing the zeta potential of organic colloids.

The slight increase in organic carbon with increased salinity from the calcium chloride solution was evidently

due to a small amount of organic carbon associated with the calcium chloride solution.

Material separated by the calcium chloride solution was about 40% volatile.

Figure 19 shows that magnesium solution produces more coagulation of kraft effluent than calcium solution but is far less effective than sodium solution. The material separated was about 45% volatile. Magnesium hydroxide was identified in the separated material by the addition of an alkaline solution of p-nitrobenzeneazoresorcinol. Based on the solubilities of magnesium compounds the presence of the hydroxide was expected.

The shape of the curves in Figure 19 are somewhat unusual. It appears that a decreasing amount of material was separated with each succeeding increment of added salinity until the inorganic carbon was exhausted. A large sudden increase in separated material then occurred.

No significant removal of organic carbon occurred with the coagulated material. Essentially all color was removed with the material, as was the case with sodium and calcium solutions. The material separated with the calcium and magnesium solutions appeared to be a white powder onto which colored material was adsorbed. No crystalline structure or separate tan colored substance similar to that produced with sodium solution was present.

Experiment 5. Experiment 5 involved an evaluation of the effect which the coagulation of kraft effluent by sea water has on the settling of suspended solids. Results of this experiment are shown in Figure 20. These data were obtained by mixing several concentrations of kraft effluent with sea water or distilled water, stirring each mixture at 15 rpm for 30 minutes, allowing quiescent settling for 30 minutes, carefully decanting the upper 50% of the mixtures and finally filtering the decanted portion for suspended solids analysis.

A curve showing the suspended solids initially present was derived from the suspended solids value for Sample 6 from Table 1. The small amounts initially present in the sea water or distilled water were neglected.

In the range of 10 to 20% by volume of kraft effluent the suspended solids in the supernatant of the two types of mixtures were about the same. The amount of suspended solids initially present in the sea water probably offset any removal due to coagulation in this range. At a kraft effluent concentration greater than 20% coagulation by sea water caused an increase in the settling rate of suspended solids. The additional amount of about 5.5 mg/l which was settled due to coagulation represents a 22% increase over that occurring in distilled water. Volatility of retained material ranged from 100% at 10% kraft effluent

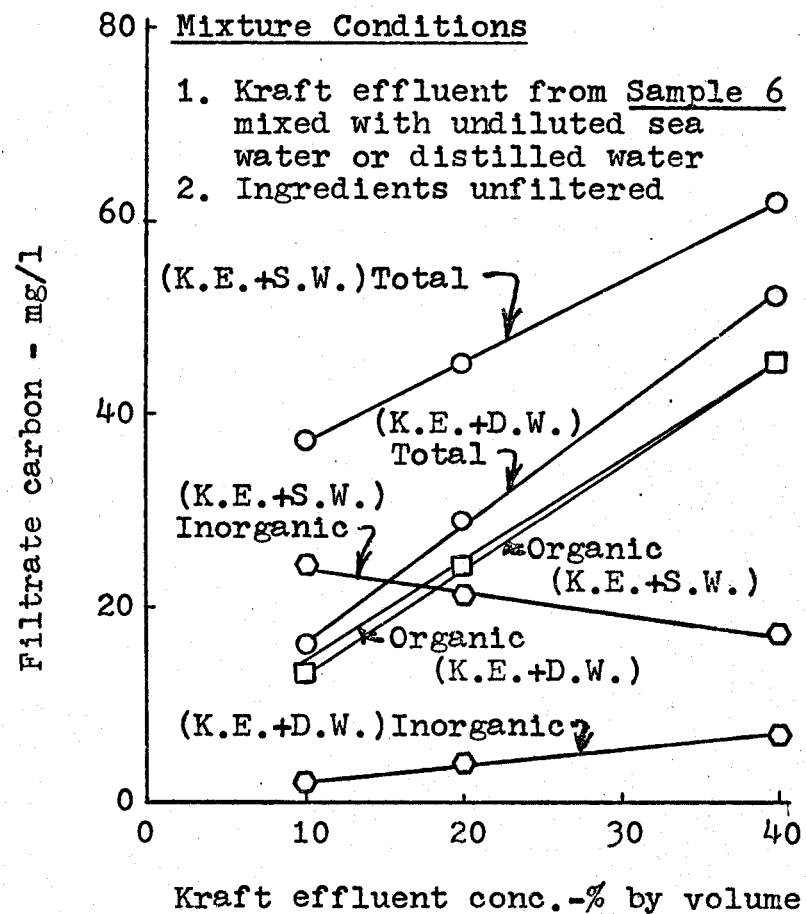
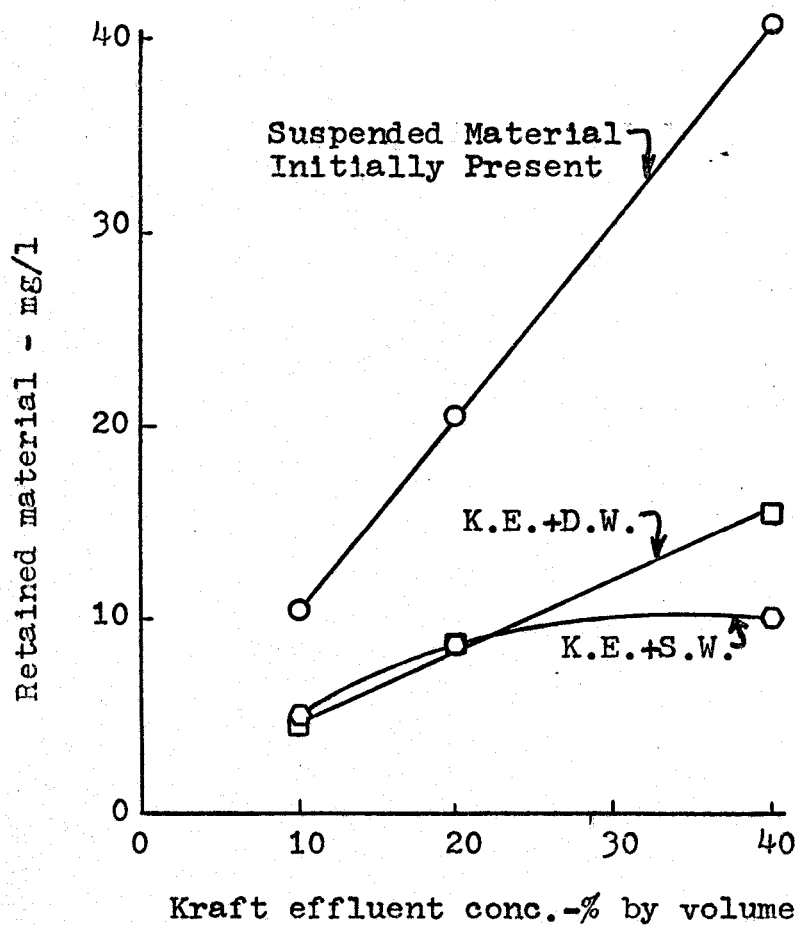


Figure 20. Retained material and Filtrate carbon versus Kraft effluent concentration

concentration to about 85% at 40% kraft effluent concentration.

Replacement of sea water by kraft effluent, which is lower in inorganic carbon, accounts for most of the decrease in filtrate inorganic carbon that occurs with increasing kraft effluent concentration in the sea water mixtures. The increase in inorganic carbon which occurs in the distilled water mixtures is due to that present in kraft effluent.

Experiment 6. The effect which a change in pH has upon the amount of material coagulated was evaluated in Experiment 6 and results are shown in Figure 21. A mixture of 20% by volume of kraft effluent in sea water has a pH of about 8.3. Adjustment of mixture pH values to those shown by plotted points was done immediately after combining the ingredients. The volatility of separated material decreased from 100% at pH 1.0 to 70% at pH 7.0 to 35% at pH 11.0. This indicates an increase in the amount of inorganic material separated at higher pH values. Essentially all color was removed with the coagulated material.

It is significant to note that no removal of organic carbon occurred with the coagulated material. An initial decrease in inorganic carbon was followed by an increase as the mixture became more alkaline. This was probably due to the absorption of carbon dioxide.

When a mixture containing 20% by volume of kraft effluent from Sample 1 and sea water was allowed to flocculate



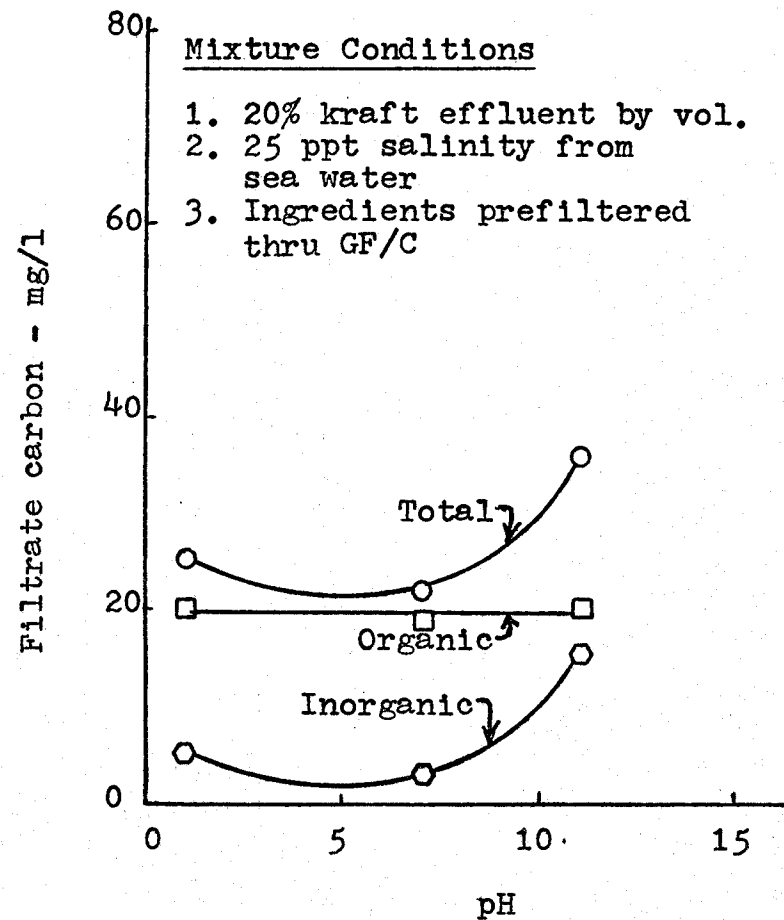
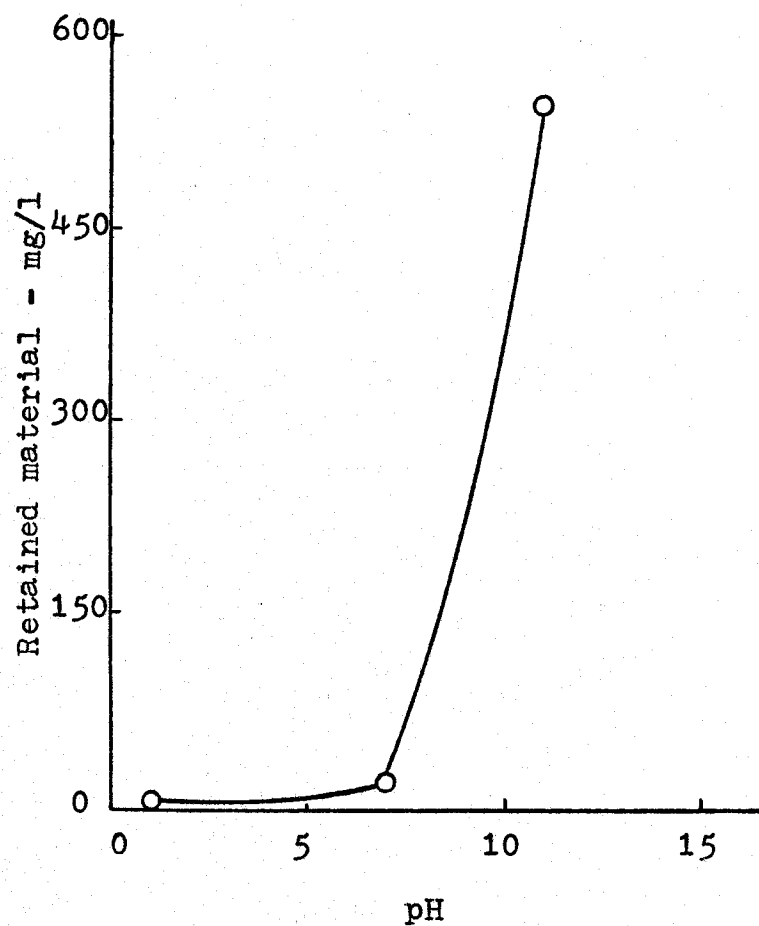


Figure 21. Retained material and Filtrate carbon versus pH

before adjusting the pH, an immediate increase in size and number of floc took place when the pH was suddenly lowered to about 1.0. In mixtures containing kraft waste from other samples, lowering the pH after flocculation did not produce a noticeable change in floc. This effect was probably dependent upon the amount of lignin contained in the different effluent samples. Sample 1 has a much higher COD than the others and therefore may have contained substantially more lignin.

In mixtures containing unfiltered ingredients about 950 mg/l of material was retained upon filtering through GF/C media after adjusting the pH to 11.0. So voluminous was the coagulated material that difficulty was experienced in filtering 250 ml of these mixtures through a 9.0 cm filter pad.

#### Characterization of Material Coagulated from Kraft Effluent By Sea Water

The fine-grained, tan colored material which is coagulated in mixtures containing filtered kraft effluent and sea water was examined for nitrogen content. Because of the small amounts of material coagulated, it was necessary to digest the fiber glass filter pads with the retained material. A clean filter pad was similarly treated and served as a blank. No nitrogen was found in the coagulated material.

No sodium was detected in the coagulated material when a sample was flamed or when zinc uranyl acetate solution was added.

A test for magnesium was made by adding an alkaline solution of p-nitrobenzeneazoresorcinol to a sample of the coagulated material. This test indicated no magnesium was present.

The tan coagulated material was found to be insoluble in acetone, benzene, chloroform, hexane and acidified hexane.

Digestion in sulphuric acid of glass fiber filter pads and retained coagulated material resulted in the formation of a black residue on the pads. As mentioned in the discussion of sodium chloride coagulated material, this is an indentifying characteristic of acid insoluble (Klason) lignin.

The addition of mineral acid to the coagulated material produced no evolution of gas. This was an indication of the absence of carbonate or bicarbonate.

## SUMMARY

Effluent from the kraft pulping and papermaking process consists of carriage water in which variable amounts of wood components, pulping chemicals and papermaking materials are dissolved or suspended. A considerable variation in effluent properties was found among the several different 24-hour composite samples used in coagulation tests during this investigation. An aging of effluent samples was noted whereby a progressive adsorption of fine material onto larger particles took place.

O'Neal (1966) reported that a flocculation of material occurred in mixtures of kraft effluent and sea water and suggested a possible waste treatment mechanism for kraft effluent based on removal of the flocculated material. The investigation herein summarized was for the primary purposes of determining the amount and nature of material involved in the flocculation. Causative factors of the flocculation were also of interest.

Floc particles were found to consist of meshes of cellulose fibers onto which a fine-grained tan-colored material agglomerated. The tan-colored material was coagulated from kraft effluent by sea water and subsequently adsorbed onto or screened from suspension by the fiber meshes. This material was found to be an acid insoluble (Klason) lignin.

Biological activity was found not to be a causative

factor of the flocculation. The size and number of floc particles were observed to depend upon the amount of fiber and other suspended material in the kraft effluent. In mixtures of filtered ingredients the number and size of floc decreased with pore size of filter media. When all fiber was removed from the kraft effluent before mixing with sea water, the resulting coagulated material consisted of very small particles which did not readily settle from suspension.

Heating of ingredients before mixing aided in flocculation of mixtures of unfiltered ingredients but did not noticeably affect mixtures of filtered ingredients.

The amount of material coagulated in various mixtures was measured as a function of time, effluent concentration, salinity and mixture pH. Individual sources of salinity included sea water and several different solutions of those salts containing some of the most prevalent elements in sea water.

It was found that coagulation was essentially completed within 30 minutes after combining ingredients. There was a general increase in the amounts of material coagulated with increases in kraft effluent concentration and salinity.

The amount of material coagulated from kraft effluent by sea water was found to vary among different samples of effluent. A maximum amount of about 2 mg/l of material was coagulated in mixtures of filtered ingredients, at kraft effluent concentrations as high as 40% by volume and

salinities contributed by sea water up to 25 ppt by weight. About twice this amount was coagulated in similar mixtures of unfiltered ingredients. Removal of coagulated material produced no significant change in mixture total alkalinity, pH, carbon content or color. Coagulation did produce a 22% increase in the amount of suspended solids settled from mixtures of unfiltered ingredients after 30 minutes of quiescent standing.

Increasing the pH of mixtures of kraft effluent and sea water has a pronounced effect upon the amount of material separated. As much as 550 mg/l was separated from mixtures of filtered ingredients upon raising the pH to 11.0. The corresponding amount for mixtures of unfiltered ingredients was about 950 mg/l. No reduction in organic carbon accompanied this voluminous separation of material.

Solutions of sodium chloride, calcium chloride and magnesium sulfate were also used as coagulants. The effectiveness in separating material was, in increasing order, calcium chloride, magnesium sulfate and sodium chloride. The sodium solution also produced the largest removal of organic carbon, about 9 mg/l at a salinity of 80 ppt. The effectiveness of the pure salt solutions in producing coagulation was much greater than equivalent ionic concentrations in sea water. This suggests that in sea water the salts may not be nearly as ionized as in pure solution.

Essentially all color was removed from mixtures with material separated by the salt solutions.

## CONCLUSIONS

This investigation has led to the following conclusions:

1. Properties of kraft effluent vary considerably among different 24-hour composite samples. An aging of the effluent results in progressive adsorption of fine sized material onto larger suspended material.
2. Sea water causes a limited coagulation of kraft effluent. Coagulation is essentially complete within 30 minutes after combining the two ingredients. The pH of mixtures has a significant effect upon the amount of material separated.
3. The material coagulated in kraft effluent by sea water is an acid insoluble (Klason) lignin. The amount of lignin coagulated varies considerably among different composite samples of kraft effluent and increases with mixture salinity and effluent concentration. Removal of coagulated material causes no significant change in mixture pH, carbon content, color or total alkalinity.
4. The lignin coagulated in mixtures of kraft effluent and sea water flocculates with cellulose fiber. Heating of ingredients aids in flocculation of mixtures containing fibers. The number and size of floc formed depends upon



the amount of fiber in suspension. An approximate 20% increase in settling of suspended solids from mixtures containing fiber results from the flocculation. In the absence of fiber the lignin coagulates to form very small particles which do not settle readily.

5. Biological activity is not involved in the flocculation.
6. Pure salt solutions coagulate kraft effluent much more effectively than equivalent concentrations of the salts in sea water. Of three salts tested, sodium chloride is most effective as a coagulant, followed by magnesium sulfate and calcium chloride. Nearly all color is removed by all three salts.
7. Coagulation of kraft effluent by sea water does not remove enough material to serve as a practical treatment method.

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