GEOTHERMAL RESERVOIR WELL STIMULATION PROGRAM

FRACTURING FLUID EVALUATION
(LABORATORY WORK)

Prepared for

U.S. DEPARTMENT OF ENERGY

CONTRACT NO. DE-AC04-79AL10563

By

VETTER RESEARCH

JANUARY 1982

REPUBLIC GEOTHERMAL, INC.
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DISCLAIMER

Report: Fracturing Fluid Evaluation (Laboratory Work)

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Abstract:
This report describes work done to characterize by chemical methods the temperature/ time degradation behavior of polymer based fluids that may be used in stimulating geothermal wells by fracturing. The polymers tested were hydroxypropulguar (HP guar), hydroxethylcellulose (HEC), carboxymethylcellulose (CMC), and XC Polymer. Also two commercially available cross-linked HP guar systems were tested.

The report covers the development of analytical techniques for characterizing the polymers and the results of static and dynamic high temperature aging of the polymers in various salt water environments. The fluids were tested at 150, 200, and 250°C. The report covers the implications of these results based on the time/ temperature degradation of the polymers and the relative ease of removing the degraded polymer from a sandpack.

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2.0 CONCLUSIONS

1. Analytical methods were developed for examining the chemical degradation of water soluble polymers.
2. Test procedures were developed for examining the high temperature static and dynamic degradation of water soluble polymers.
3. It was found that overall, the frac fluid systems (which contain various additives) have as good or better stability and clean-up than the "pure" polymer fluids.
4. Of the polymer solutions, HEC had the best stability and clean-up.
5. All the fluids had good stability up to 150°C but only the commercial frac fluids had good displacement characteristics.
6. None of the fluids were found to be stable at 250°C.
7. The effect of the salts on stabilizing the polymer degradation was dependent on the particular polymer and test temperature. No overall conclusion could be reached on a salt effect on polymer degradation.
8. The titanium cross-linker formed an insoluble precipitate of titanium oxides at 150°C. This loss of cross-linker, while affecting viscosity, should not have a negative effect due to formation of the solid residue.
9. Holding the polymer fluids in the sandpack for 48 hours resulted in a greater amount of polymer being retained in the sandpack.

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PREAMBLE

Republic Geothermal, Inc. (RGI) is the prime contractor under DOE/DGE Contract No. DE-AC04-79AL10563. This contract is concerned with the stimulation of geothermal reservoir wells. Vetter Research (VR) is a subcontractor for RGI and is charged with chemical and material investigations and evaluations under this DOE/DGE prime contract. VR is managing subcontract DE-AC04-79AL10563-VR under the prime contract.

This report is being issued under subcontract No. DE-AC04-AL10563-VR and is related to the chemical investigation of the degradation of polymer fluids that may be used in geothermal well fracturing.

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3.0 INTRODUCTION

An economical geothermal well depends on having an adequate sustained flow of fluid from the formation at high temperatures. In order to improve this flow from marginal wells, it has been proposed to "borrow" some oilfield technology for well stimulation. One technique being investigated is that of formation fracturing using polymer thickened water carrying various propping agents. Since there has been very little work done on the degradation of these polymers at temperatures to 150°C, it was felt that a research project looking at temperatures to 250°C would be worthwhile to both examine any potential problems with these materials and to select the optimum fluid for geothermal fracturing.

3.1 THE FUNCTIONS OF POLYMERS IN FRACTURING FLUIDS

Polymers are used in fracturing fluids for proppant suspension, friction reduction, and fluid loss control. Most fracturing fluids contain some solids (usually a certain mesh size sand) that will lodge in the open fracture to prop it open after the fracturing pressure is released. The frac fluid is required to have sufficient viscosity to suspend this proppant and deliver it into the fracture. Polymers are added to maintain this required viscosity. Frac fluid formulations have a negative effect in that they can increase the horsepower needed to pump the fluid into the wellbore and fracture the formation. Other polymers can then be used to reduce the friction factor of the fluid thereby causing reduced horsepower requirements to pump the fluid.

Lastly, some polymers work with the fine mesh particles added to frac fluids to reduce the amount of water that is lost to the formation by the high differential pressures used in fracturing.

After performing these functions, the polymer fluid should degrade in a manner that reduces its viscosity with no residual insoluble particles. The viscosity should be lowered enough to allow the fracturing fluid to flow back to the surface and be "cleaned" from the fracture.

3.2 POLYMER TYPES USED IN FRACTURING FLUIDS

The most prevalent polymer now used in fracturing fluids is hydroxypropylguar gum. Other polymers used include guar gum, xanthan gum, hydroxyethylcellulose, carboxymethylcellulose and various acrylates and acrylamides. Since the main thrust of the project is to look at technology and products that are being used in current practice, it was decided to only examine those polymers that make up the bulk of the current useage in the field. Since acrylates and acrylamides are used in relatively minor amounts in fracturing fluids, they were not examined for this project. The following section describes in detail the four polymers and two fracturing fluid systems used for these tests.

3.2.1 HYDROXYPROPYLGUAR GUM

Of the polymers used in hydraulic fracturing, the greatest percentage is in the form of hydroxypropylguar gum (HP guar). HP guar is formed by reacting guar gum (a naturally occurring material derived from the seed of the guar plant) with propylene oxide. The propylene group then substitutes onto one or more of the OH-sites (Figure 1, is a diagram of the guar gum repeating unit).

It is a non-ionic, high molecular weight polysaccharide. The term polysaccharide refers to polymers that are mainly composed of different sugar molecules. The addition of the propylene group improves the solubility and clarity, and lessens the amount of degraded residue compared with the pure guar gum.

HP guar is relatively inexpensive and gives good rheological properties in solution. Its viscosity is greatly enhanced by cross-linking with borate or various heavy metals. It is subject to bacterial enzymatic degradation and requires some type of preservative. HP guar is used for both viscosity and fluid loss control.

3.2.2 CELLULOSE GUMS

Two types of cellulose gums were used for these tests, carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC). Figure 2 shows the chemical structure of a modified cellulose polymer. Many sites on the cellulose backbone can be reacted to form the alkyl substituted cellulose. The "R" in Figure 2 refers to either the hydroxyethyl or the carboxymethyl group. The amount and type of alkyl group substituted on the backbone determines the solubility and rheological characteristics of the polymer.

These two polymers are also high molecular weight polysaccharides. The CMC is anionic and the HEC is non-ionic. They are both used for viscosity and fluid loss control and can be cross-linked by heavy metals. They are more expensive than HP guar. They can be degraded enzymatically but do not normally require additions of preservatives.

3.2.3 XC POLYMER

XC Polymer is a high molecular weight naturally occurring polysaccharide called xanthan gum made by the fermentation of the bacteria Xanthamonas campestris. XC polymer is a more complex, anionic material whose generally accepted structure is shown in Figure 3. It is more expensive than the other polymers tested but is generally used at lower concentrations. Its main function in fracturing fluids is for viscosity and friction reduction. It can be degraded bacterially only with great difficulty and does not normally require a preservative.

3.2.4 COMMERCIAL FRAC FLUID SYSTEMS

Two commercially available HP guar systems were also examined in the laboratory. They are referred to as System A and System B and are essentially composed of the following:

System A - 40 lb/1000 gal HP guar
Buffering agents
Titanium complex cross-linker

System B - 60 lb/1000 gal HP guar
Buffering agents
Titanium complex cross-linker
2% KCl

3.3 POLYMER DEGRADATION

Polymers are chemical entities that are composed of repeating units of a basic molecular structure (see Figures 1 through 3) called a monomer. These are linked together to form the long chain structures of the polymer. The physical properties seen in polymer solutions are the result of the length of the chain, the side arms on the chain, the association or bonding between the chains, and the type of monomers.

Degradation occurs as the side arms and the long chains are broken. These chains can be broken chemically, biologically, or thermally. In the usual order of degradation, the long chain is first broken into the monomeric units, the monomeric units are broken into their constituent sugar molecules, and lastly these sugar molecules are broken into their various chemical components. The polymer will "break" initially at the weakest chemical connection and it then takes increasing time and/or energy input (i.e., temperature) to reduce the polymer to its individual chemical components.

As mentioned previously, frac polymers are structurally very complex. The various ways in which they can decompose are equally complex and as a result numerous products of decomposition are to be expected. Much of the presently available literature on their degradations deals with biochemical (i.e., enzymatic) degradation. While this literature is applicable to frac polymer breakers containing enzymes, it does not apply to frac polymer breakdown from chemical or thermal reactions. Because of the high temperatures found in geothermal reservoirs, these are the reactions most frequently occurring. Unfortunately, these are also the most complex reactions to characterize because of the numerous courses the degradation may follow. It is not surprising that little is known about their chemistry.

The decomposition of cellulose and its derivatives (see Figure 2) can be used to illustrate the complexity of the problem.

Points A through E in Figure 2 indicate expected points of chemical attack during polymer decomposition. Depending on conditions, decomposition can occur at any or all of these points to give a broad spectrum of decomposition products. The conditions and products expected for each point of attack are as follows:

A. Enzymatic cleavage of a terminal sugar unit on the polymer chain to give the intact chain, less one sugar unit. Because enzymes normally do not survive high temperature conditions, it is doubtful that this reaction occurs in geothermal operations.

B. Hydrogen atom abstraction caused by the presence of free radical type initiators. The most common initiator is oxygen and in the presence of oxygen, complete degradation of the polymer to carbon dioxide and water will occur. Since frac polymers are used under reducing conditions (i.e., no oxygen) free radical degradation, when it occurs, is induced by interaction of the frac polymer with initiators other than oxygen. Typical free radical initiators would be certain transition metal ions existing in the formation (e.g., Fe++). These can either be dissolved in the reservoir fluid or contained on the surface of formation material.

C. Side chain degradation is normally expected during the early stages of degradation of most frac polymers. The major product of concern with polymers such as CMC and HEC is cellulose, which is a water insoluble material. Side chain degradation can occur in most polymers under conditions much milder than those encountered in geothermal wells and will usually result in some loss of their viscosifying properties. High amounts of shear (i.e., mixing or high pumping rates) can cause side chain degradation in most polymers.

D. Backbone cleavage comes about from hydrolysis or free radical induced degradation of the polymer at some point along the polymer chain. The hydrolysis reaction is accelerated under acid conditions and is usually slower when the polymer has been chemically modified along the side chains or has very complex side chains. In either case of degradation, the initial reaction products are polymer chains of lower molecular weights. This results in solutions of increasingly lower viscosity.

E. Polymer dehydration is responsible for the burnt or caramel type odor and color observed when water is lost from the polymer chain. This occurs when R = H in Figure 2 and frequently results in a solid residue.

3.3.1 IDEAL DEGRADATION OF FRACTURING FLUIDS

Ideally, a fracturing fluid is formulated to certain viscosity and fluid loss specifications which will be maintained as the fluid is held on the surface, the proppant is added, and the fluid is pumped downhole to open a fracture. After the fracture is opened the proppant must be released to hold it open. This is accomplished by both slowing the fluid and by loss of viscosity as the polymer degrades.

After the fracturing procedure is completed, the viscosity of the fluid should decrease to a value close to that of the produced fluid so that the produced fluid (either oil, gas, or geothermal water) can flush the remains of the polymer from the reservoir and wellbore.

Also, ideally, as the polymer degrades chemically the degradation products will be completely water soluble so that there is no retention of insoluble residues in the fracture other than the solid proppants.

3.3.2 VISCOSITY DEGRADATION

Many times the viscosity of a polymer fluid will break too soon thereby causing the proppant to settle in the wellbore and perhaps plug the hole or the perforations. This may be especially true of geothermal wells with the high temperatures the fluid will experience being pumped downhole. Usually, a large volume of cool water (prepad) is injected prior to the frac fluid so that this problem is minimized.

The rheological properties of the fluids have been studied by Maurer Engineering as a separate part of this contract and the results reported separately. A brief discussion of this data related to the findings in this report is covered in Section 7.0.

3.3.3 CHEMICAL DEGRADATION

As the polymer fluid degrades into its chemical constituents, not all of it forms completely soluble materials as is ideally desired. All the polymers now being used for hydraulic fracturing will, under certain conditions, form insoluble products. These products may then either physically plug or chemically associate with the formation or proppants to effectively reduce the flow of fluid from the formation. These insoluble products, called residue, are different for each polymer type and relate to the basic chemical structure of that polymer.

3.4 PURPOSE OF THIS LABORATORY STUDY

The purpose of the laboratory study described in this report is to chemically analyze the degradation under geothermal conditions, of currently available fracturing fluids, and to determine if the degradation products of the selected polymers may pose any problems for the production of geothermal waters. To do this, a set of analytical procedures was developed for analyzing these high molecular weight polymers, and a set of experiments was performed to examine the degradation of the polymers under static and dynamic conditions simulating geothermal operations.

4.0 DEVELOPMENT OF ANALYTICAL PROCEDURES

There has been a lack of chemical methods available in the past to properly characterize high molcular weight, water-soluble polymers as they degrade. A major part of this contract was spent developing the analytical procedures needed to better determine the rate of degradation and the degradation products of the polymers. These procedures were then used to characterize the laboratory fluids as well as the fluids used in the field during field experiments.

4.1 CARBOHYDRATE AND TOTAL ORGANIC CARBON ANALYSIS

There were two methods developed and used in this study for determining the gross chemical changes in degraded polymers. These are analyses for the total carbohydrate content (CHO) and the total organic carbon (TOC) content. These values are related to each other by the quantity of organic carbon in the carbohydrate. Typically, carbohydrates are about 40% carbon. If the polymer degrades to soluble organic materials, and the system is closed so that no organic materials escape by volatilization, the CHO content will approach zero but the TOC will remain constant. Therefore, by following the CHO/TOC ratio a direct indication of the polymer degradation can be seen. At 40% TOC concentration, the CHO/TOC ratio would be 2.5. As the carbohydrate degrades, the TOC content remains the same; therefore, this ratio will approach zero as the polymer degrades to noncarbohydrate, soluble material. Plots of the CHO/TOC ratios are used in this report to determine relative degradation rates of the polymers tested.

4.2 ADVANCED INSTRUMENTAL METHODS OF CHEMICAL CHARACTERIZATION

Of the advanced methods of instrumentally characterizing chemical compounds, all must take into consideration the chemical nature of the species to be characterized. In the case at hand, the expected degradation products:

a. are water soluble,

b. contain only carbon, hydrogen and oxygen, and

c. must be analyzed under conditions that they are stable.

Several methods were considered and it was concluded that the more subtle measurements of the structural and molecular weight changes involved in the degradation of polymers could be followed by high pressure liquid chromatographic (HPLC) analysis.

While some progress was made in applying HPLC techniques, insufficient time was available to fully explore the technique. Appendix A describes in detail the development work on the equipment and procedures leading to the analysis of the frac polymers described in this report. Hopefully, this information can be used as a basis upon which future work can be done.

The HPLC analysis works by examining the retention time of the polymer solution as it is flowed at a constant rate through a closely packed column. In general, the degradation of a polymer results in conversion to lower molecular weight units which cause longer retention time in the HPLC column.

As discussed in the Appendix, it was found that accurate retention times could only be obtained for polymer solutions in deionized water. Although much headway was made in delineating the problems associated with using brine waters and frac fluids with HPLC techniques, much more time and effort would be necessary to fully develop it to analyze actual field fluids. This method, however, still holds the most promise for quantifying the actual structural changes in the polymer as it degrades. These changes are the most important ones in relating degradation to changes in viscosity.

5.0 LABORATORY DEGRADATION TESTS

As mentioned previously, the purpose of this work was to characterize the degradation of currently available fracturing fluid products when they are used at geothermal temperatures. To accomplish this, the work is divided into two parts - static aging tests and dynamic (flow) tests.

5.1 STATIC AGING TESTS

This series of tests was designed to examine the time/temperature effects on the degradation of \frac polymers in the presence of formation materials and various salt waters. Table 1 shows the matrix set up for these tests. This matrix resulted in 90 separate aging tests with 540 samples being pulled for analysis, including testing two commercially available frac fluid systems.

Each sample was analyzed for TOC and CHO content and was observed for any discoloration or insoluble material present. The deionized water samples were also analyzed by HPLC. Preliminary resu

5.1.1 TEST EQUIPMENT AND SAMPLING FOR STATIC TESTS

The equipment used for conducting the static aging tests is shown schematically in Figure 4. It consists of a stirred reaction vessel constructed of Hastelloy C (a nickel based metal highly resistant to brine corrosion) connected to a pressurized sample collector in an ice bath. The initial sample in the reaction vessel was pressurized well above the vapor pressure of water at the test temperature. The sample collector was pressurized at or above this vapor pressure but lower than the reaction vessel. In theory a sample could then be removed at the required time intervals without flashing the liquid. In practice some flashing did occur as will be discussed later. These samples were then kept in the refrigerator until all testing was complete.

5.1.2 TEST PROCEDURE

The procedure for sample preparation and testing is as follows:

- Mixing - The polymers were all mixed at 0.25 wt % in a Waring blender for 5 minutes in either deionized water or the salt water in which the test would be run. The pH's were all adjusted to 7.0 and the samples were de-aired by an aspirator. The commercial fluids were mixed by following the explicit directions submitted by the manufacturer. The fluids were used immediately after preparation.

- Aging and Sampling - The samples were then placed into the test vessel and nitrogen was bubbled through them to remove as much oxygen as possible and a nitrogen gas cap was left over the fluid to run the test. The test cell was then placed in a pre-heated jacket and the test fluid was heated to the desired temperature. Samples were then taken at 30 minutes, one-, three-, six-, and 22-hour intervals after having reached the test temperature. Throughout the aging period, the stirrer was running.

5.2 DYNAMIC AGING TESTS

The static tests were designed to test the time/temperature relationship of the polymer degradation. Of particular interest are the detrimental effects of degradation products on flow through the sandpacks (i.e., increases in pressure drop) and the retention of degradation products in the sandpack after flushing with fresh brine.

5.2.1 TEST EQUIPMENT

Figure 5 shows the schematic diagram for the dynamic tests. One reservoir is filled with the polymer fluid and the other is filled with the brine water for flushing the sandpacks. The metering pump is a constant rate HPLC pump manufactured by Altex. Pressure transducers were installed on each side of the sandpack for continuous differential pressure readings and an automatic sample collector was used for sampling.

5.2.1.1 SANDPACK

A special sandpack holder was constructed for these tests by Autoclave Engineers Inc. Figure 6 shows a schematic of a sandpack cell. It is constructed with all wetted parts of Hastelloy C and consists of a 3/4-inch pipe nipple with specially designed high pressure seals on the ends. Each end cap has a recess for placement of sintered Hastelloy C frits to hold the sand in place. The cell is connected on each end to 1/8-inch Hastelloy C tubing which leads to shut-off valves outside the oil bath. The special sealing arrangement at each end of the sandpack consists of a gland nut and retaining ring that causes a metal-to-metal seal on the machined contact surfaces.

The 20/40-mesh sand used for these tests was dry packed by pouring increments of sand into the holder, packing each increment with a hammer and wooden dowel. The pore volume in the sandpack was checked by injecting water into a vertically held sandpack with the constant rate pump. The time of arrival of the water to the top of the holder was then converted to the pore volume inside the sandpack. This volume was found to be about 18.6 cc (an average taken from ten samples).

The dimensions of the empty holder are 20.5 cm long with a 1.72 cm inside diameter. This gives an empty volume of about 47.7 cc. This then, gives the porosity of the sandpack of at least 39%.

5.2.1.2 THICKENING OF HIGH TEMPERATURE SILICONE OIL

A special high temperature silicone oil was obtained for the oil baths in these tests. The first silicone oil (Dow Corning 200 Fluid) obtained worked well at 150°C, but after a few days' heating at 200°C, it polymerized, forming a semi-solid gelatinous mass that had to be scraped from the oil bath. Two to three man-days were required to put the oil bath back into operation.

A second silicone oil was obtained (Dow Corning 710) which has a reported upper temperature limit of 260°C. According to the Dow Corning literature, even this fluid has a finite life of a few hundred hours at this temperature.

In addition, it was found that at temperatures above 200°C, the oils gave off an irritating volatile substance which necessitated building fume hoods over each oil bath.

5.2.2 TEST PROCEDURE AND ANALYSIS

The same polymers and temperatures were used for the dynamic tests as were used for the static tests (see Table 1). For these tests the total fluid was tested for TOC and CHO as it was eluted from the sandpack. Therefore, a material balance could be made for each test as well as the degradation characteristics.

The following procedure was used:

1. Pack column with 20/40 mesh Brady frac sand and determine approximate pore volume.

2. Flow polymer through sandpack for about 10 pore volumes (sandpack immersed in high temperature oil bath) at 1.0 cc/min.

3. Immediately flush with brine water for one hour and 15 minutes collecting samples every 15 minutes. (Flow rate 1.0 cc/min.)

4. Repeat step number 2.

5. Shut in sandpack for 48 hours at the test temperature.

6. Reflush with brine water for three hours, collecting samples as in step 3.

The system was continuously monitored for pressure build-up during all tests described above.

The flow rate of 1.0 cc/min. was an arbitrary number chosen to fit the timing desired for the test procedure. Actual fracturing flow rates vary greatly from job to job so it would be difficult to choose a "typical" flow rate to use for these tests. The only detrimental effect to the degradation results would be a very high flow rate resulting in extra mechanical shear being placed on the polymer. Some polymers do degrade with shear to some extent, but the polymers used in this study have been found to be very stable to shear. The only effect found in subjecting these polymers to high shear has been some reduction in viscosity or change in their basic rheological characteristics, probably as a result of changes to, or loss of, side chains. The degradation experienced due to the temperatures used in these tests far overshadow any degradation that may come about by submitting the polymers to high shear.

High flow rates can also affect the displacement of the polymers from the sandpacks. However, since the viscosity of the fluids has more effect on the relative mobilities than the flow rate, and since the viscosities of these fluids all have approached that of water at these temperatures, it was felt that this flow rate would still give adequate displacement data.

This procedure resulted in 15 different tests and 285 separate samples for analysis.

6.0 TEST RESULTS

The test results are divided into three sections: the static results, the dynamic results, and the degradation/viscosity relationships. The final section will consolidate these results and make some recommendations for polymer use in geothermal fracturing.

6.1 STATIC AGING TESTS

Descriptions of the TOC and CHO analysis for each polymer tested are discussed in the next sections followed by a discussion of the overall effects of salt water, temperature, and time.

6.1.1 PRESENTATION OF STATIC DEGRADATION RESULTS

As discussed in Section 4.1, the percentage degradation of the polymers was followed by analyzing the samples for TOC and CHO content and then calculating the CHO/TOC ratio. However, this ratio is not a constant value and varies for each polymer tested. For example, the CHO/TOC ratio for XC Polymer is 2.43 while the ratio for CMC is 2.57. Therefore, to be able to more easily compare the degradation of each polymer, the data is presented as a percent reduction from the original CHO/TOC value. This was calculated by dividing the CHO/TOC value at each sample time by the original CHO/TOC value from zero time. The discussions in the body of the report will use the term percent (%) degraded which means the percent of the original CHO/TOC ratio to which the polymer has been reduced.

6.1.2 SIGNIFICANCE OF DEGRADATION RESULTS

As discussed in Section 3.3.2, the ideal fracturing fluid is, in general, expected to degrade after the time period necessary to complete the frac job so that it can be more easily removed. This time period is dictated by many factors involved in fracturing design. Therefore, it is difficult to pick "good" or "bad" degradation results from the graphs presented here. For example, if a well is fractured, the pumping is stopped, and the well flowed within an hour or two, then the polymer should be well degraded by that time. However, if it takes eight hours to fracture and place the proppant and the well will be shut in for 24 hours, then obviously a rapid degradation is not required. In fact, it may be detrimental. Therefore, these graphs should not necessarily be used for absolute values but only to compare the relative degradation of each of the polymers, the relative effects of salt waters on the degradation, and as a guide to their possible use in geothermal operations.

6.1.3 CMC RESULTS

Figures 7, 8 and 9 show the degradation based on the percent change of the CHO/TOC ratio during the static aging of this polymer.

Increasing temperature markedly increased the rate of degradation of the CMC. The samples all degraded less than 50% at 150°C. At 200°C they had all degraded by more than 50% after three hours, and at 250°C they had degraded more than 50% by 0.5 hours.

The effect of the salts on stabilizing the CMC degradation was inconclusive. At 150°C, CMC was more stable with high concentrations of both sodium and calcium chloride. At 200°C, CMC was more stable in DI water and high salt solutions than it was in solutions of low salt concentration. At 250°C it was more stable with both high and low concentrations of sodium chloride.

6.1.4 HEC RESULTS

Figures 10, 11 and 12 show the results of the static aging tests with HEC. Overall the HEC seemed to have better stability than the other polymers tested. It remained fairly stable at 150°C, but degraded steadily at 200°C and 250°C. In general, the HEC fluid prepared in deionized water was more stable than those prepared with the salts. At 150°C all the salts lowered the stability of the HEC slightly. At 200°C the 1000 mg/l CaCl2 solution had a detrimental effect on the stability. At 250°C, both CaCl2/HEC solutions had lower stabilities than the other fluids. At 150°C, after an initial degradation of 10% to 20% during the first one to three hours, the stability of the HEC remained constant. At 200°C there was a gradual decrease in the stability of the polymer with increasing time. At 250°C there is a rapid decrease (greater than 50% degradation) in the stability during the first two to three hours, then a gradual decrease for the remainder of the test. The CaCl2 treated fluids, however, had totally degraded within six hours.

6.1.5 XC POLYMER RESULTS

Figures 13, 14 and 15 show the results of the degradation tests for XC polymer. In general, the XC polymer had excellent stability at 150°C and poor stability at 200 and 250°C. At 200°C the polymer was 50% degraded within six hours, and at 250°C it was 50% degraded within one-half hour. The addition of salts was inconsistent as to whether or not it helped to retard the degradation of the polymer. At 150°C salt additions seemed to accelerate the degradation. At 200°C it retarded degradation, and at 250°C it had no effect.

6.1.6 HP GUAR RESULTS

Figures 16, 17 and 18 show the results of the tests on HP guar. In general, HP guar had moderate to poor stability in these tests. At 150°C all but the deionized water sample had less than 40% degradation throughout the test. The additions of sodium chloride seemed to enhance the stability. At 200°C there was a 20% to 40% degradation of the polymer within the first hour of the test, then a gradual loss throughout the rest of the test. Salt additions did not seem to have a significant effect on the stability. At 250°C the polymer degraded rapidly (85 to 90% degraded) within one to two hours.

6.1.7 FRAC FLUID RESULTS

Figure 19 shows the results of the static tests run on the two frac fluids. Both of these fluids are based on HP guar and, therefore, should show similar degradation characteristics. Frac Fluid A was more stable than HP guar at 150 and 200°C and similar to HP guar at 250°C. Frac Fluid B was only run at 150°C for the static tests and had similar stability to HP guar. These systems were prepared in deionized water.

6.1.8 EFFECT OF TEMPERATURE

As expected, increasing temperatures increased the degradation rate of the polymers. The HEC seemed to be less affected by the temperature increases than the other polymers. The degradation between 150 and 200°C was not as great as the increase in degradation in going from 200°C to 250°C for most of the polymers.

6.1.9 EFFECT OF TIME

Longer elapsed time at a given temperature in most cases showed increased degradation especially at 200 and 250°C. At 150°C, the HEC and XC polymers were fairly stable with time. At 200°C, except for HEC, most of the polymer degradation had taken place within one and six hours. HEC had only a gradual degradation over the 22-hour test period (see Figure 11). At 250°C most of the degradation would take place in the first two hours.

6.1.10 EFFECT OF SALTS

The effect of salts on stabilizing the degradation of the polymers showed no distinct trend. It varied with the different polymers and with the test temperature. Salt additions seemed to increase stability in the following cases:

1. CMC at 150°C had higher stability with high concentrations of both sodium and calcium chloride.
2. CMC at 250°C had higher stability with both concentrations of sodium chloride but not with calcium chloride.
3. XC polymer at 200°C had higher stability with both salts at both concentrations.
4. HP guar at 150°C had higher stability with sodium chloride at both concentrations.

HEC, which had, in general, better stabilities than the other polymers, seemed to have lower stabilities upon salt additions.

6.1.11 RESIDUE

In some cases a light to dark brown insoluble residue appeared in the samples. This material was determined to be a carbonaceous material and was formed by the degraded polymer, probably by a dehydration mechanism as discussed in section 3.3. Although some discoloration of the samples was noted, no particles were observed until the 200°C samples were taken. At 200°C this residue appeared after thirty minutes in the HP guar sample, after one hour in the Frac Fluid A and after six hours in the other samples. At 250°C the residue appeared immediately in the HP guar and Frac Fluid A samples, and after one hour in the others.

6.1.12 DISCUSSION OF STATIC DEGRADATION

The effects of time and temperature on the degradation of polymers was very straightforward. Increases in either parameter gave higher degrees of degradation of all the samples tested. This relates directly to breaking the "backbone" (the basic long chain) of the polymer. As this degradation proceeds the end products are individual sugar molecules which are water soluble. In addition to breaking the long chain, the sugar units were evidently dehydrating, forming an insoluble carbonaceous material (the dark brown particles, section 6.1.11). In essence this is "burnt sugar" and is an undesirable by-product of the degradation of the polymers particularly if it leads to formation damage.

The effect of salts on the degradation of the polymers is not as straightforward. In general, the literature discusses salt effects on these polymers only with respect to viscosity changes, gel formation and precipitation. The published data has little to do with the degradation of the polymers. Salts can have an effect on degradation by either accelerating or retarding their breakdown. This would occur by either weakening or protecting the sites on the molecular chain that are the most susceptible (see section 3.3) to cleavage. Another protective mechanism would be inter-chain bonding between the individual molecular chains making a more rigid structure, thereby inhibiting the breaking apart of the long chain molecule such as occurs during cross-linking.

The series of tests in this report seem to indicate that mono and divalent cations (sodium and calcium) have little effect or at least no consistent effect on the degradation of the polymers. But, comparing the data from the two frac fluids with the HP guar data indicates that the additives in the frac fluids (which contain a trivalent cation, Ti+++) does impart protection to this polymer. Based on the known chemistry of titanium complexes, this stability is due in part to the chemical interaction of the titanium ion with functional groups on the polymer. There is no evidence of analogous chemistry of either sodium or calcium in the literature.

6.2 STATIC AGING TESTS DISCUSSION

Table 2 gives a comparison of the static degradation studies based on the half-life of the CHO/TOC ratio of each polymer. The half-life is defined as the time required for CHO/TOC ratio to reach 50% of its original value.

An examination of this table shows that in general HEC had the best stability, and CMC the lowest stability of the polymer solutions. However, the commercial Frac Fluid A was even more stable than the HEC based on its 200°C half-life of greater than 22 hours.

The following is a ranking of the fluids tested based on their overall stability (Frac Fluid B is not included since it was only run at 150°C):

Frac Fluid A
HEC
HP guar
XC polymer
CMC

6.3 TITANIUM PRECIPITATION

The cross-linking agent used in the two commercial frac fluids is an organic titanium complex. An analysis of some residue from the static test of the frac fluids showed the presence of titanium. Consequently, a test was run on aging a sample of the cross-linking solution at 150°C in deionized water.

Within thirty minutes this sample had formed a milky white precipitate that was approximately 70% titanium (electron probe analysis). This material in all probability is composed of oxides of titanium. Considering the small amount of cross-linking agent used in these fluids (less than 0.1% by wt), this precipitate would probably cause no problems in the formation. However, its relatively rapid precipitation could be part of the reason for the rapid loss of viscosity of these fluids as they are heated.

6.4 DYNAMIC TESTS

The presentation and description of the results of the dynamic tests described in Section 5.2 are in the following sections.

6.4.1 PRESENTATION OF DYNAMIC DEGRADATION RESULTS

The tables and graphs used to show the results from the dynamic tests are in two sections. The first section is similar to the static results being presented as polymer degradation based on the change in the CHO/TOC ratio. The second is a material balance based on the TOC flushed from the sandpack by the displacement of the polymer with brine water. Each graph of the dynamic test results is divided by a dashed line representing the 48-hour time period that the sandpack is shut-in (Figures 20 through 27). The left side of the dashed line shows the first polymer injection sequence into the sandpack. As soon as ten pore volumes of polymer were injected into the sandpack, it was flushed with brine water. The sandpack was immediately reinjected with the polymer and then shut-in for 48 hours. The right side of the graphs (0 to 3 hours) presents the data from analyzing the fluids after being shut-in the sandpack for 48 hours. The water used for displacement in all the dynamic tests was a 3000 mg/l TDS brine water.

6.4.2 DEGRADATION RESULTS UNDER DYNAMIC CONDITIONS

Figures 20 through 25 and Tables 3 and 4 show the results of the dynamic degradation tests. In general, the degradation under dynamic conditions confirmed the results from the static tests. HEC again showed the most stability compared to the other polymers.

6.4.2.1 CMC RESULTS

Figure 20 shows the results of the degradation of CMC under dynamic conditions. This polymer had the widest variation in percentage degradation of any of the polymers tested. The initial phases of flow both at 150°C and 200°C contained measureable amounts of degraded polymer solutions. Then after about 40 minutes of flow (about 2.5 pore volumes), less degraded polymer was observed in the effluent. This displacement pattern was repeated after the 48 hour shut-in period but to a less dramatic extent.

The qualitative shape of the return curve for CMC indicates that the sandpack is periodically producing fluids of continuously increasing and decreasing amounts of polymer relative to the total organic carbon content of the effluent. Similar, but much less pronounced discontinuities were seen in the effluents from the other polymer systems (cf. Figures 21-25). While it could be argued that these discontinuities are experimental artifacts related to channeling or "breakthrough" in the sandpack, the internal consistency of CMC data with its relatively large discontinuities at both 150° and 200°C do not favor this argument.

Instead, it is suggested that the variations in the CHO/TOC ratio with flow can be related to regions in the sandpack containing solutions of varying viscosity. These regions can be caused by either localized degradation or non-uniform mixing of the displacement fluid with the frac fluid originally introduced into the sandpack. As a result, flow through and out of the sandpack is not homogeneous.

6.4.2.2 HEC RESULTS

Figure 21 shows the degradation of HEC under dynamic conditions. The initial flow shows degradation of the polymer similar to that seen in the static tests. However, after the 48-hour shut-in period the HEC had degraded severely at 200°C and had degraded completely at 250°C (no CHO return from the sandpack). No polymer was returned from the sandpack during the 48-hour test after one hour at 150°C and after 1.75 hours at 200°C. There was some degraded polymer being returned at 250°C throughout the flow period although at a very low level.

6.4.2.3 XC POLYMER RESULTS

Figure 22 shows the results of the dynamic degradation of XC polymer. These results are similar to the results obtained from the static tests. It is interesting to note that no polymer was being returned for 15 minutes after about 1.5 hours' flow from the sandpack after the 48-hour shut-in. Then the next 15 minutes had polymer return and then it stopped returning for the duration of the test.

6.4.2.4 HP GUAR RESULTS

Figure 23 shows the degradation of HP guar under dynamic conditions. The results seem to confirm the static degradation results. Also, HP guar, like the other polymers, stopped being displaced from the sandpack during the 150°C, 48-hour shut-in test.

6.4.2.5 FRAC FLUID RESULTS

The dynamic degradation of Frac Fluid A is shown in Figure 24 and Frac Fluid B in Figure 25. Frac Fluid A seemed to have less degradation during the initial flow at 150°C than was indicated during the static tests (dynamic 90% to 100%, static 80% to 90% CHO/TOC ratio). Also, after 48 hours' shut-in at 200°C, this fluid had degraded to about 10% CHO/TOC ratio which is much more degradation than would be indicated by the static tests (about 70% after 22 hours). This frac fluid also stopped being returned from the sandpack after flowing for a while (about 2 hours).

Frac Fluid B was tested at three temperatures since it had been selected to be used in some actual field experiments. The initial flow degradations were higher than the static and dynamic results of HP guar at 150°C and 200°C. However, as expected, the polymer in this fluid totally degraded at 250°C. It should also be noted that it is significant that this fluid, unlike any of the other fluids, was being displaced from the sandpack throughout the time period of each of the flow tests. In general, Frac Fluid B gave good results for stability and displacement.

6.4.3 POLYMER DISPLACEMENT RESULTS

Figures 26 and 27 and Tables 3 and 4 show the results of the percent of polymer removed from the sandpacks during the flow tests. This displacement is based on a material balance of the TOC content of the polymers. Since all of the liquid displaced from the sandpack was collected and analyzed, this should be a very accurate measure of each polymer's tendency to be left in the sandpack. This is very important in that it is an indication of possible particle plugging problems from the polymer.

6.4.3.1 DISPLACEMENT RESULTS AT 150°C

The best removal from the sandpack was accomplished by Frac Fluid B at 80% and 78% TOC removed (Table 3). Frac Fluid A had excellent displacement initially (98%) but was poor after the 48-hour aging (41%). It is interesting to note that HP guar is the polymer in both these frac fluids, yet it had relatively poor TOC recovery (44% and 23%). Both the XC polymer and HEC seemed to have good displacement (although lower than Frac Fluid B) while CMC and HP guar were judged to have poor displacement.

6.4.3.2 DISPLACEMENT RESULTS AT 200°C

The relative rankings of the polymers for displacement at 200°C is about the same as at 150°C except for the HP guar (Table 4). The HP guar seemed to have much better displacement at 200°C than at 150°C. Again, the best would be the Frac Fluid B followed by HEC and XC polymer.

6.4.3.3 DISPLACEMENT RESULTS AT 250°C

Frac Fluid B and HEC were also tested at 250°C. The percent TOC recovery of these tests is as follows:

	Initial	48-Hour
HEC	17.7	25.1
Frac Fluid B	55.6	27.6

These data seem to indicate that as the temperature increases, the ability of a polymer to be cleaned from a sandpack is greatly impaired. In any event, it would probably take much longer to flush the polymer from the sand (and by inference, from the formation) at the higher temperatures.

6.4.3.4 DISCUSSION OF PRESSURE DATA FROM DYNAMIC TESTS

While injecting and flushing the polymer fluids from the sandpacks, a continuous measurement of the total flowing pressure and differential pressure across the sandpack was made. Since there was a back pressure regulator installed in the flow system, the flowing pressure on the liquid was maintained above the vapor pressure of water at the test temperature. These pressures ranged from 117 to 147 psig at 150°C, 234 to 273 psig at 200°C, and 600 to 630 psig at 250°C. The differential pressure (P) measured across the sandpack was recorded to show any possible plugging tendencies of the polymers either as they were being injected into or being flushed from the sandpacks. While flowing only the brine water through the sandpack (before injecting any polymer) the differential pressure was zero. Tables 5 through 7 show the results from the differential pressure measurements. Table 5 shows the pressure differential across the sandpack during the first injection of each polymer. The data marked with an asterisk are averages of two different tests. Only HEC had zero injection pressure at each test temperature. It should be pointed out that these increases in pressure could be due to build-up of the polymers on the 40-micron frit in the end cap that holds the sand in place. However, it is still significant that the HEC gave no restrictions while flowing through the frit.

Table 6 shows the differential pressure across the sandpack while the flow is reversed and the polymers are being displaced. Neither CMC nor HEC had any differential pressure while being displaced. The others required some pressure to initiate flow, but then went to zero pressure fairly rapidly. Only Frac Fluid A at 200°C required some differential pressure for a substantial time period (95 minutes).

Table 7 shows the pressures required for the second injection of the polymers into the sandpacks. These results were similar to the first injections except that neither cellulosic material required any pressure for injection.

After aging for 48 hours none of the fluids had any differential pressure while being displaced.

7.0 DEGRADATION RESULTS RELATED TO VISCOSITY

A report entitled Geothermal Fracture Stimulation Technology, Volume III, Geothermal Fracture Fluids issued in January, 1981, shows the high temperature viscosity measurements of the polymers and some frac fluid systems. The results of this testing showed that the physical property of viscosity is irreversibly lost at temperatures of 150°C and above for all the polymers tested in this report. However, viscosity changes in a polymer are related to solution properties (i.e., ionic bonding, physical entanglement) and structural changes which may or may not relate to actual degradation of the polymer chain itself. For example, both HEC and XC polymer degraded very little at 150°C based on the CHO/TOC ratios (about 10% degradation after 22 hours). Yet they both irretrievably lost about 75% of their viscosity (170 sec -1) after aging four hours at this same temperature (page 23, Geothermal Fracturing Fluids, Volume III).

As discussed in Section 3.0, the CHO and TOC analyses only measure gross changes in polymer degradation. The HPLC work holds the best promise for examining subtle changes in the polymer (side chain cleavage, molecular weight changes). However, attempts to do this in actual field fluids containing salt waters were unsuccessful (see Appendix). Therefore, any analysis of how degradation affects viscosity changes will have to await further development work with the HPLC. However, as shown in this work, the gross degradation and clean-up of the proppant pack or formation can be analyzed very well by the CHO and TOC determinations.

8.0 DISCUSSION OF TEST RESULTS

Based on both the static degradation and the polymer displacement tests, the commercially available frac fluid systems seemed to offer the most advantages. Evidently the additives put into the fluids can facilitate both the stability of the polymer and the removal of the polymer from the frac sand. However, the tests in this report only show additives with HP guar. Similar tests examining fluids formulated with the other polymers and additives would have to be run to see if this would generally be true.

Based on these tests, however, the following conclusions can be reached:

1. Up to 150°C any of the fluids can be used for stability but only a prepared frac fluid should be used for good displacement.
2. Between 150°C and 200°C only the commercial frac fluids (i.e., Systems A and B) had good stability and displacement.
3. None of the fluids were considered stable at 250°C.
4. Frac Fluid B had excellent displacement at all temperatures.
5. All the polymer fluids left significant amounts of material in the sandpacks.
6. The percent polymer left in the sandpack was dependent upon the time elapsed before being displaced.
7. The titanium cross-linking agent formed an insoluble precipitate upon heating to 150°C.

9.0 RECOMMENDATIONS

The further continuation of this study should be directed toward the following:

1. Examining HEC solutions with frac fluid additives. HEC had very good stability but was not displaced well from the sandpack. Various frac fluid additives may be able to improve this.
2. Examine the displacement of selected fluids from actual core materials.
3. Further development work on using the HPLC to determine structural

changes in the polymers in the presence of frac fluid additives since the HPLC is the only method known at present that can detect subtle changes in the polymers (see Appendix A).

In using polymer fluids in the field the following is recommended based on this study:

1. Displace the polymer fluid from the formation as soon as possible.
2. Use complete frac fluid systems, not "pure" polymers.

TABLE 1

FRAC FLUID STATIC AGING TESTS

POLYMERS AT 0.25 WT%	TEMPERATURES USED	TIME OF SAMPLES, HRS
XY POLYMER		0
HP GUAR	150°C	0.5
CMC	200°C	1.0
HEC	250°C	3.0
COMMERCIAL SYSTEMS		6.0
		22

MATRICES - DI WATER
DI WATER WITH EAST MESA SANDSTONE
100 AND 1000 mg/l NaCl
100 and 1000 mg/l CaCl2

TABLE 2
CHO/TOC HALF-LIFE (HOURS)
FROM STATIC AGING TESTS

	DI WATER	NaCl		CaCl		AVERAGE
		100 mg/l	1000 mg/l	100 mg/l	1000 mg/l	
CMC, 150°C	18	>22	>22	>22	>22	>22
200°C	2	0.5	1	0.5	1	1
250°C	0.5	0.5	0.5	0.5	<0.5	0.5
HEC, 150°C	>22	>22	>22	>22	>22	>22
200°C	>22	16	13	15	6	14
250°C	2	2	3	0.5	0.5	1.6
XC, 150°C	>22	>22	>22	>22	>22	>22
200°C	1	2	5	2	3	2.6
250°C	<0.5	0.5	0.5	0.5	0.5	0.5
HP GUAR, 150°C	18	>22	>22	>22	>22	>22
200°C	4	10	3	7	4	7
250°C	0.5	0.5	0.5	0.5	0.5	0.5
FLUID A, 150°C	>22					
200°C	>22					
250°C	0.5					
FLUID B, 150°C	>22					
200°C	NR					
250°C	NR					

NR = NOT RUN

TABLE 3

POLYMER DISPLACEMENT FROM THE SANDPACK*

150°C

POLYMER	WT OF TOC, mg INJECTED INTO SANDPACK	REMOVED FROM SANDPACK INITIAL	48 HR	% TOC RECOVERED INITIAL	48 HR
CMC	19.45	9.89	5.86	50.8	30.1
HEC	23.95	16.59	14.94	69.2	62.4
XC POLYMER	20.60	16.35	11.66	79.4	56.6
HP GUAR	25.65	11.29	5.91	44.1	23.0
FLUID A	44.9	44.07	18.41	98.2	41.0
FLUID B	49.36	39.57	38.7	80.2	78.4

*Displaced with 3000 mg/l sodium chloride brine

TABLE 4

POLYMER DISPLACEMENT FROM SANDPACK*

200°C

	WT OF TOC, mg			%TOC RECOVERED	
		REMOVED FROM SANDPACK			
POLYMER	INJECTED INTO SANDPACK	INITIAL	48 HR	INITIAL	48 HR
CMC	19.45	9.55	5.75	49.1	29.6
HEC	23.95	13.08	13.36	54.6	55.8
XC POLYMER	20.60	11.73	10.61	56.9	51.5
HP GUAR	25.65	19.98	11.91	77.9	46.4
FLUID A	44.9	30.08	20.36	67.0	45.3
FLUID B	49.36	35.48	37.81	71.9	76.6

*Displaced with 3000 mg/l sodium chloride brine

TABLE 5

FIRST INJECTION DIFFERENTIAL PRESSURES

		150°C	200°C	250°C
CMC,	5 min.	0.2	0.2	-
	finish	0.2	0.2	-
HEC,	5 min.	0	0*	0
	finish	0	0*	0
XC Polymer,	5 min.	0.35*	0.17*	-
	finish	0.35*	0.65*	-
HP guar,	5 min.	0	0.1	-
	finish	0	1.3	-
Frac Fluid A,	5 min.	0.2	0.6*	-
	finish	1.3	2.75*	-
Frac Fluid B,	5 min.	0.45*	0.3*	0.5
	finish	2.85*	3.0*	2.1

*Average of two runs

TABLE 6

DISPLACEMENT DIFFERENTIAL PRESSURES

		150°C	200°C	250°C
CMC,	start	0	0	-
	finish	0	0	-
HEC,	start	0	0*	0
	finish	0	0*	0
XC Polymer,	start	0.25*	0.5*	0.4
	5 min.	0*	0*	0
HP guar,	start	0.3	0	-
	10 min.	0	0	-
Frac Fluid A,	start	0.5	1.5*	-
	3 min.	0.4	0.85*	-
	10 min.	0	0.65*	-
	20 min.	0	0.3*	-
	95 min.	0	0.15*	-
	120 min.	0	0*	-
Frac Fluid B,	start	0.9*	1.5*	0.2
	5 min.	0.7*	0*	0
	20 min.	0.1*	0*	0
	50 min.	0*	0*	0

*Average of two runs

TABLE 7

SECOND INJECTION DIFFERENTIAL PRESSURES

		150°C	200°C	250°C
CMC,	5 min.	0	0	-
	finish	0	0	-
HEC,	5 min.	0	0*	0
	finish	0	0*	0
XC Polymer,	5 min.	0.1*	0.18*	-
	finish	0.5*	0.6*	-
HP guar,	5 min.	0.15	0	-
	finish	0	0	-
Frac Fluid A,	5 min.	0.16	0.15*	-
	finish	3.0	1.75*	-
Frac Fluid B,	5 min.	3.5*	2.6*	1.0
	finish	2.5*	2.7*	1.8

*Average of two runs

FIGURE 1

CHEMICAL STRUCTURE OF GUAR GUM

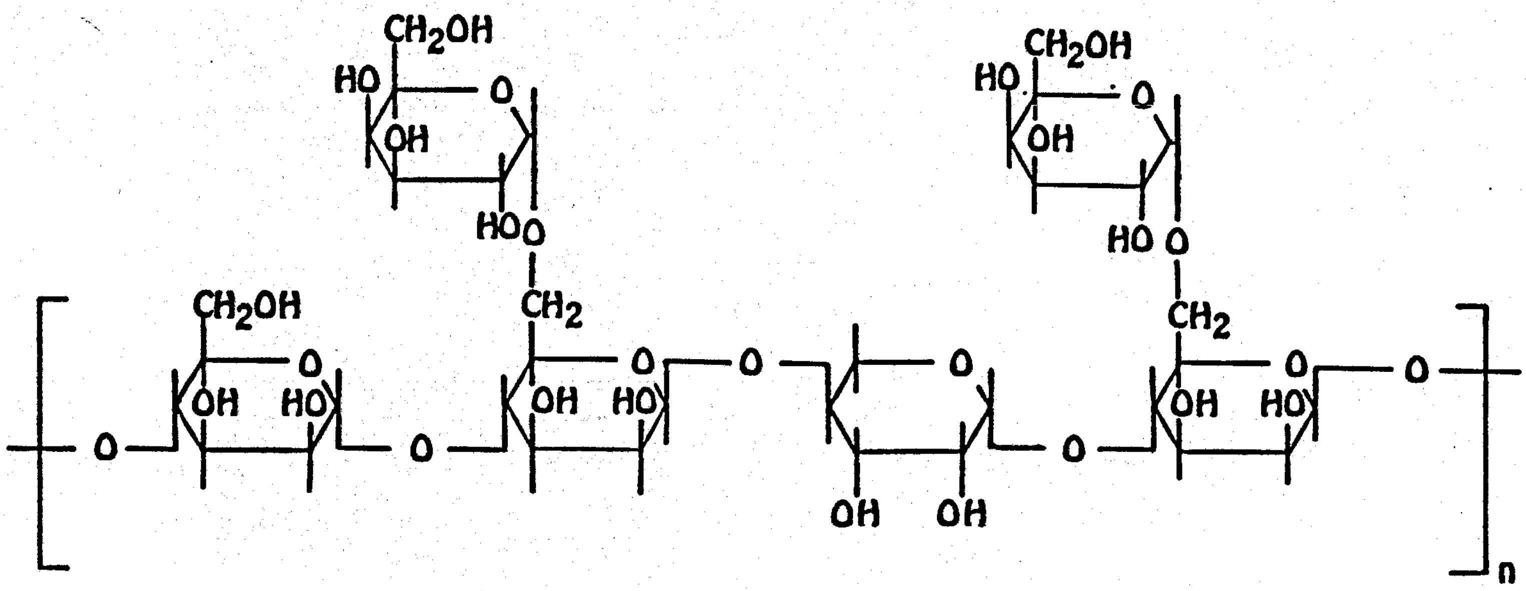
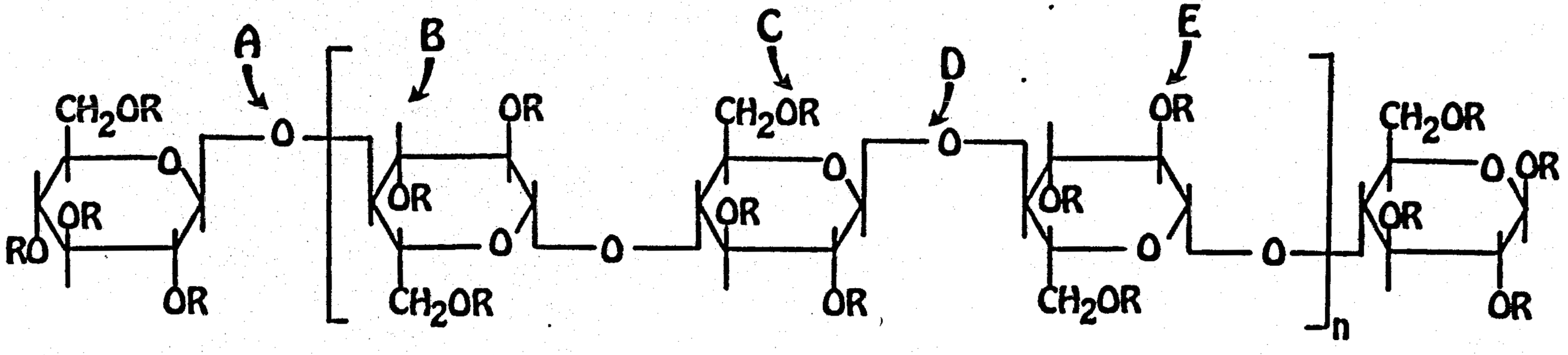


FIGURE 2

CHEMICAL STRUCTURE OF MODIFIED CELLULOSE



R: H, CH_2CH_2OH, CH_2CO_2H, etc.

FIGURE 3

CHEMICAL STRUCTURE OF XANTHAN GUM

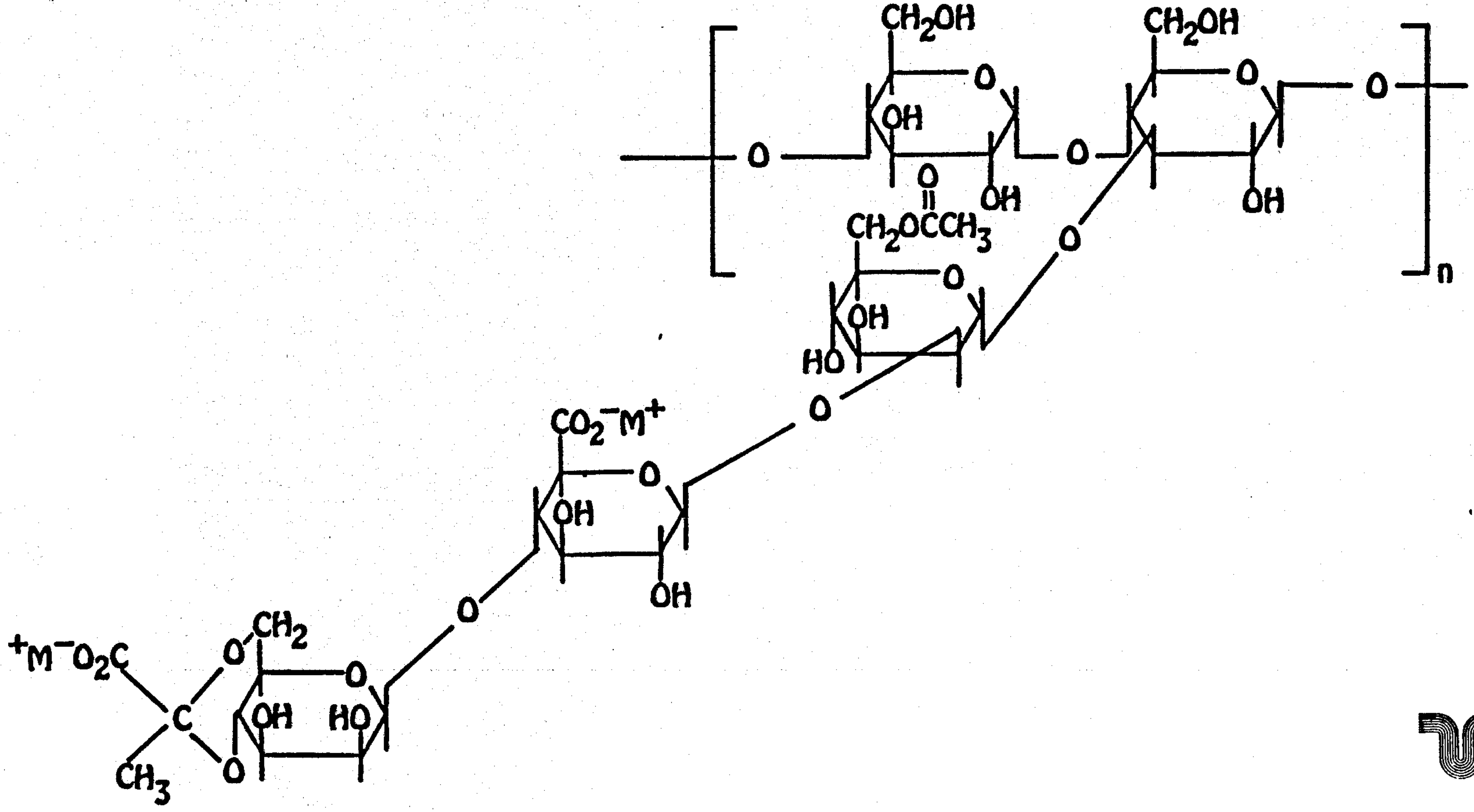


FIGURE 4

REACTION VESSEL FOR STATIC TESTS

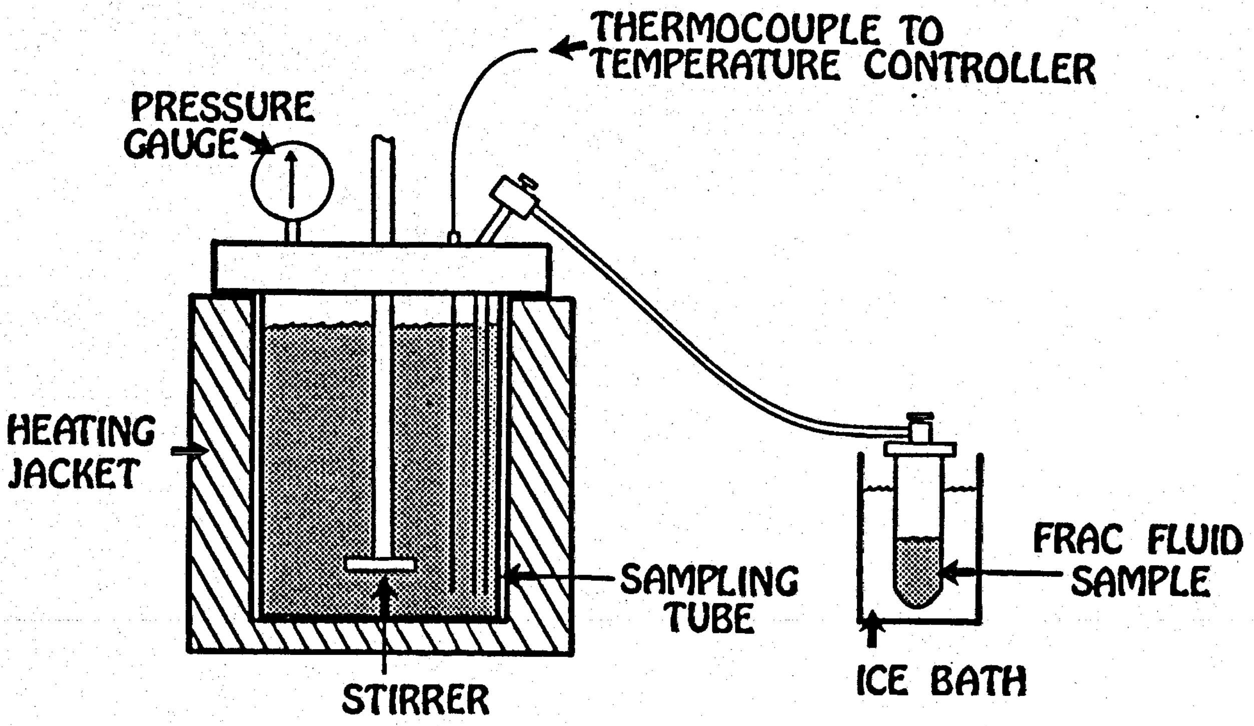


FIGURE 5

SCHEMATIC DIAGRAM OF FLOW TEST EXPERIMENTS

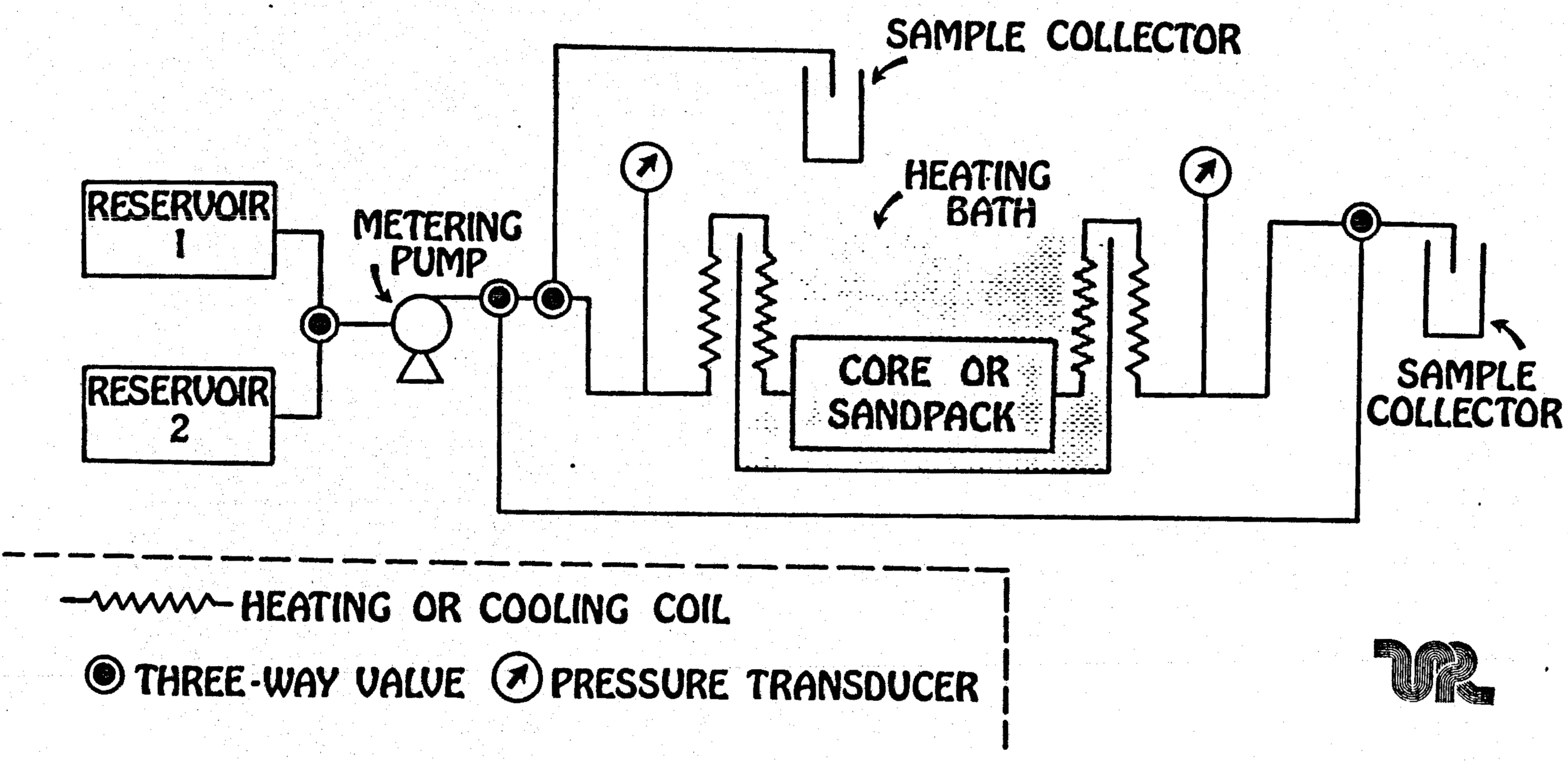


FIGURE 6

FLOW THROUGH TEST VESSEL FOR SANDPACKS

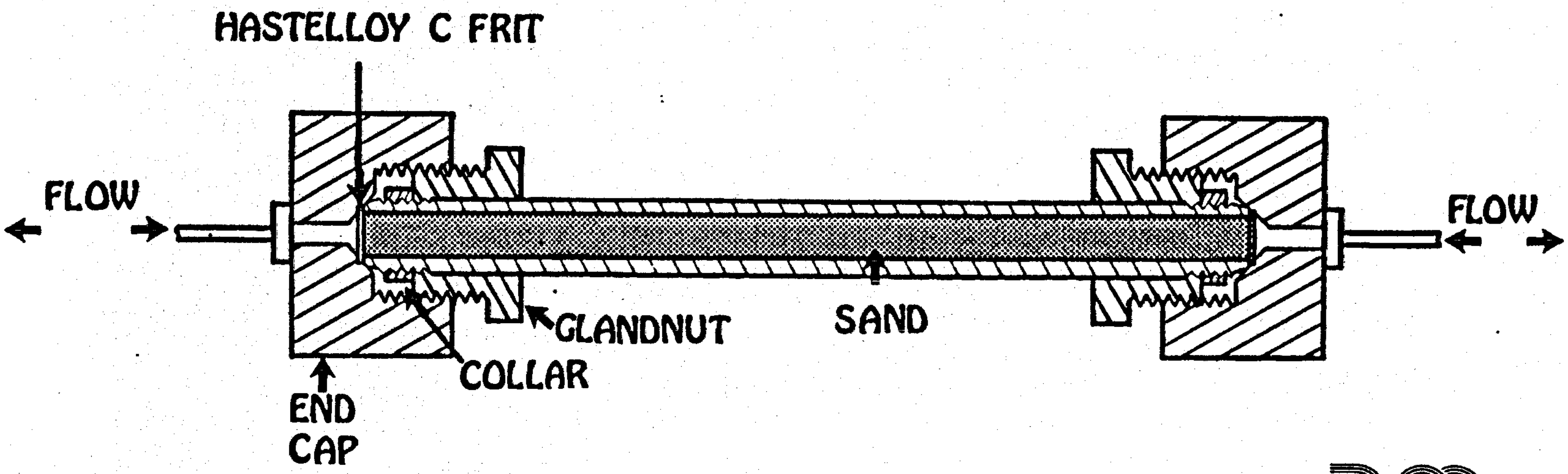


FIGURE 7

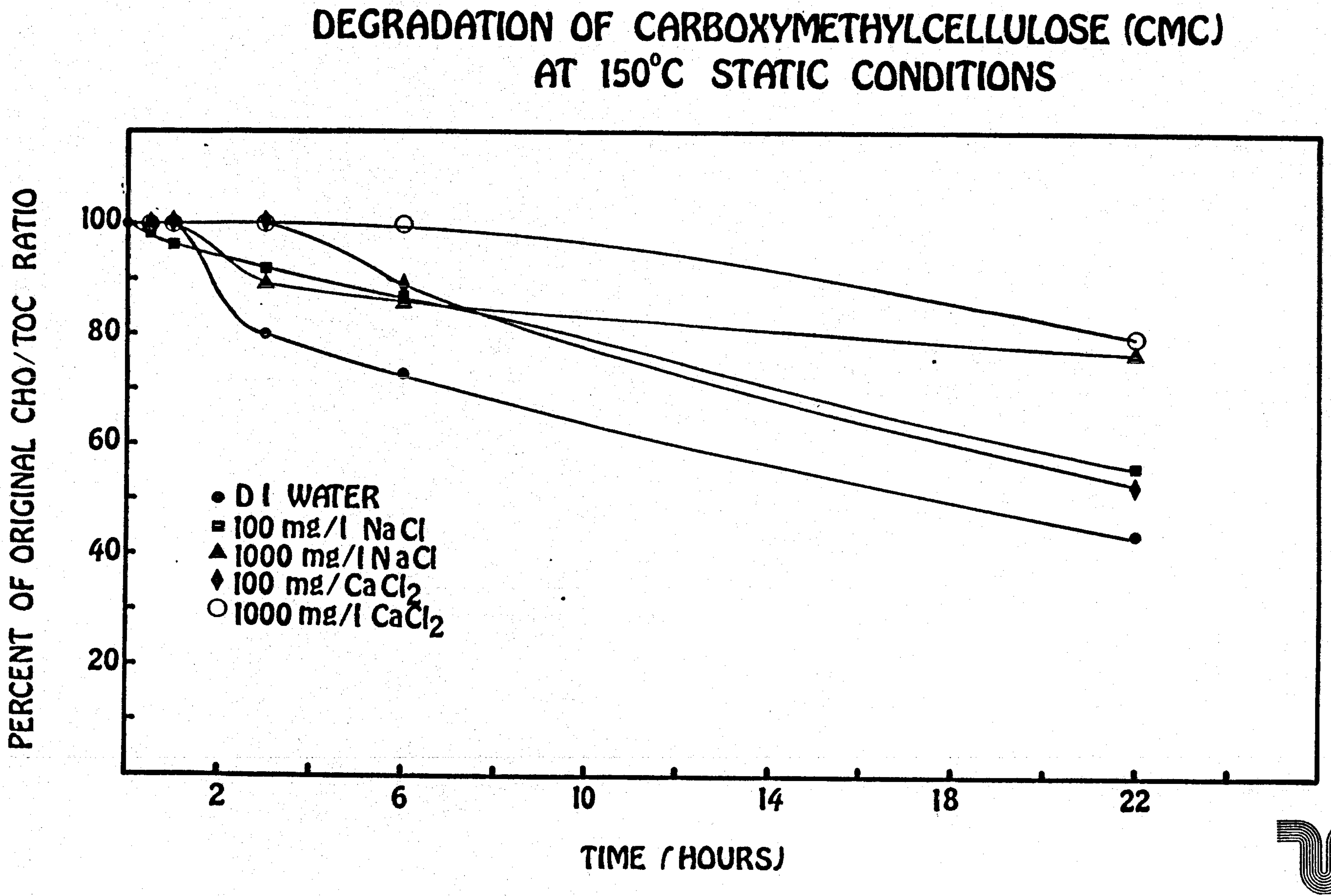

DEGRADATION OF CARBOXYMETHYLCELLULOSE (CMC)
AT 150°C STATIC CONDITIONS
PERCENT OF ORIGINAL CHO/TOC RATIO
100
80
60
40
20
2
6
10
14
18
22
TIME (HOURS)
● D I WATER
■ 100 mg/l NaCl
▲ 1000 mg/l NaCl
♦ 100 mg/CaCl2
○ 1000 mg/l CaCl2

FIGURE 8

DEGRADATION OF CARBOXYMETHYLCELLULOSE (CMC) AT 200°C STATIC CONDITIONS

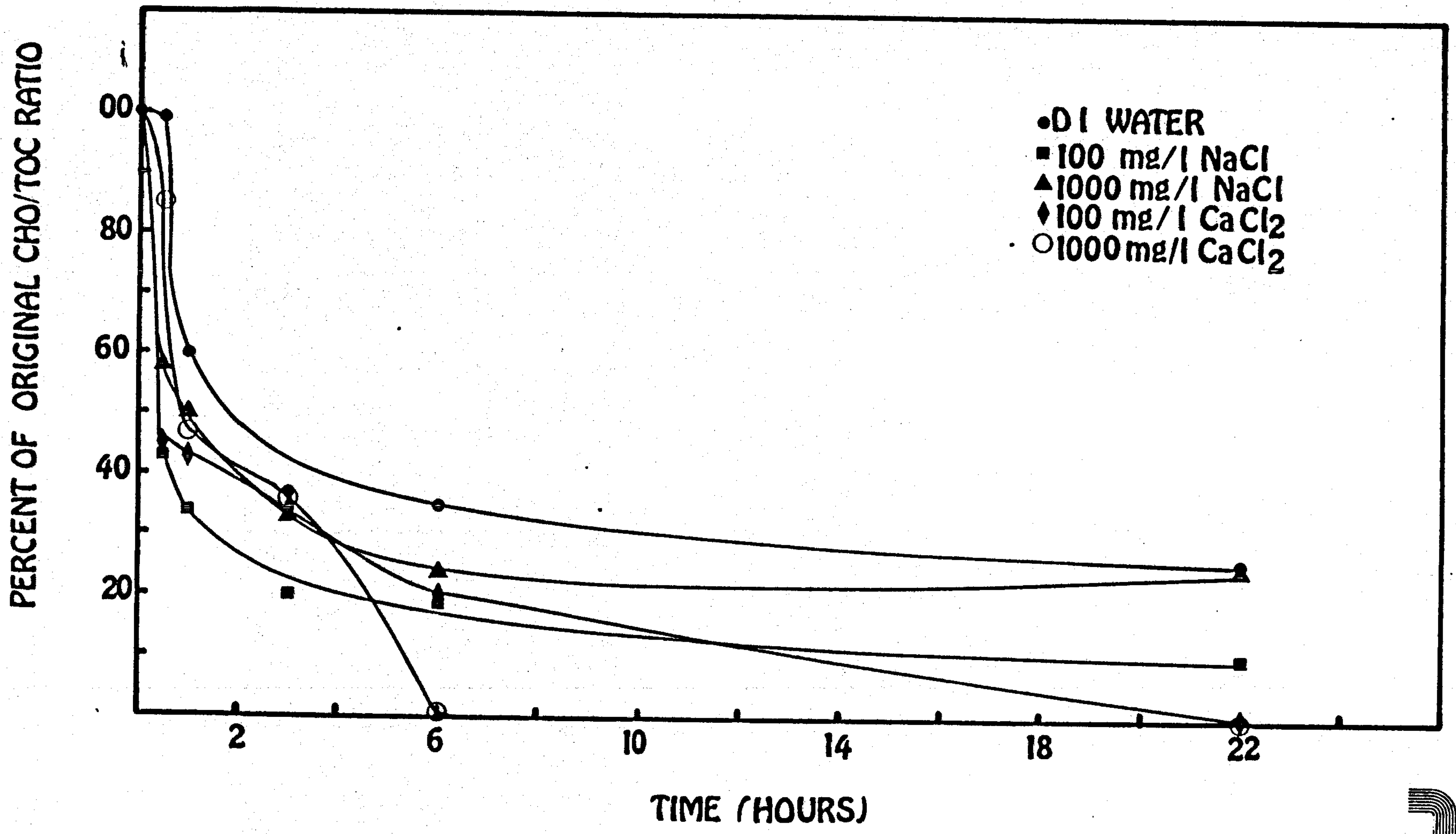


FIGURE 9

DEGRADATION OF CARBOXYMETHYLCELLULOSE (CMC) AT 250°C STATIC CONDITIONS

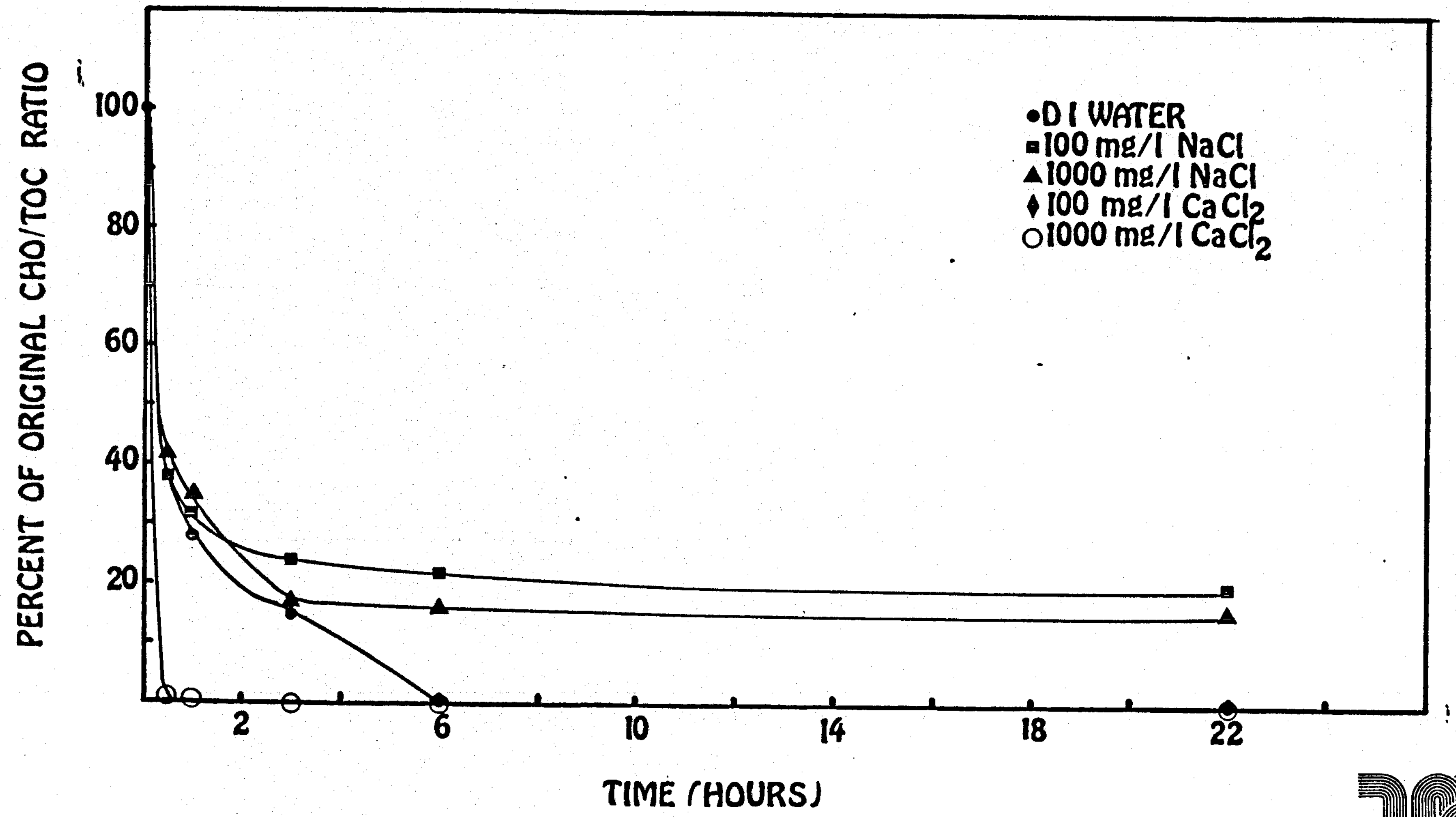


FIGURE 10

DEGRADATION OF HYDROXYETHYLCELLULOSE (HEC)
AT 150°C STATIC CONDITIONS

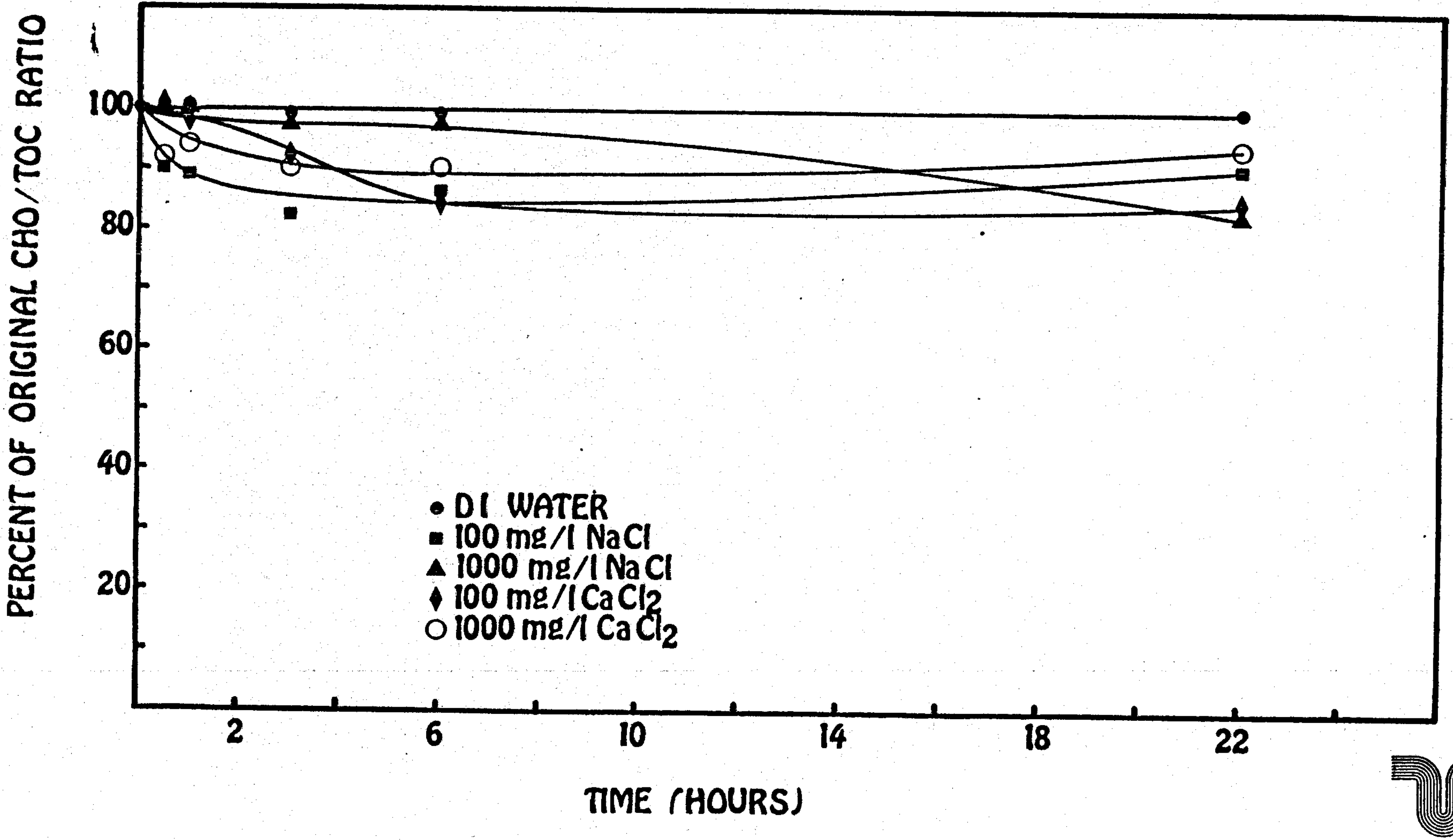


FIGURE 11

DEGRADATION OF HYDROXYETHYLCELLULOSE (HEC) AT 200°C STATIC CONDITIONS

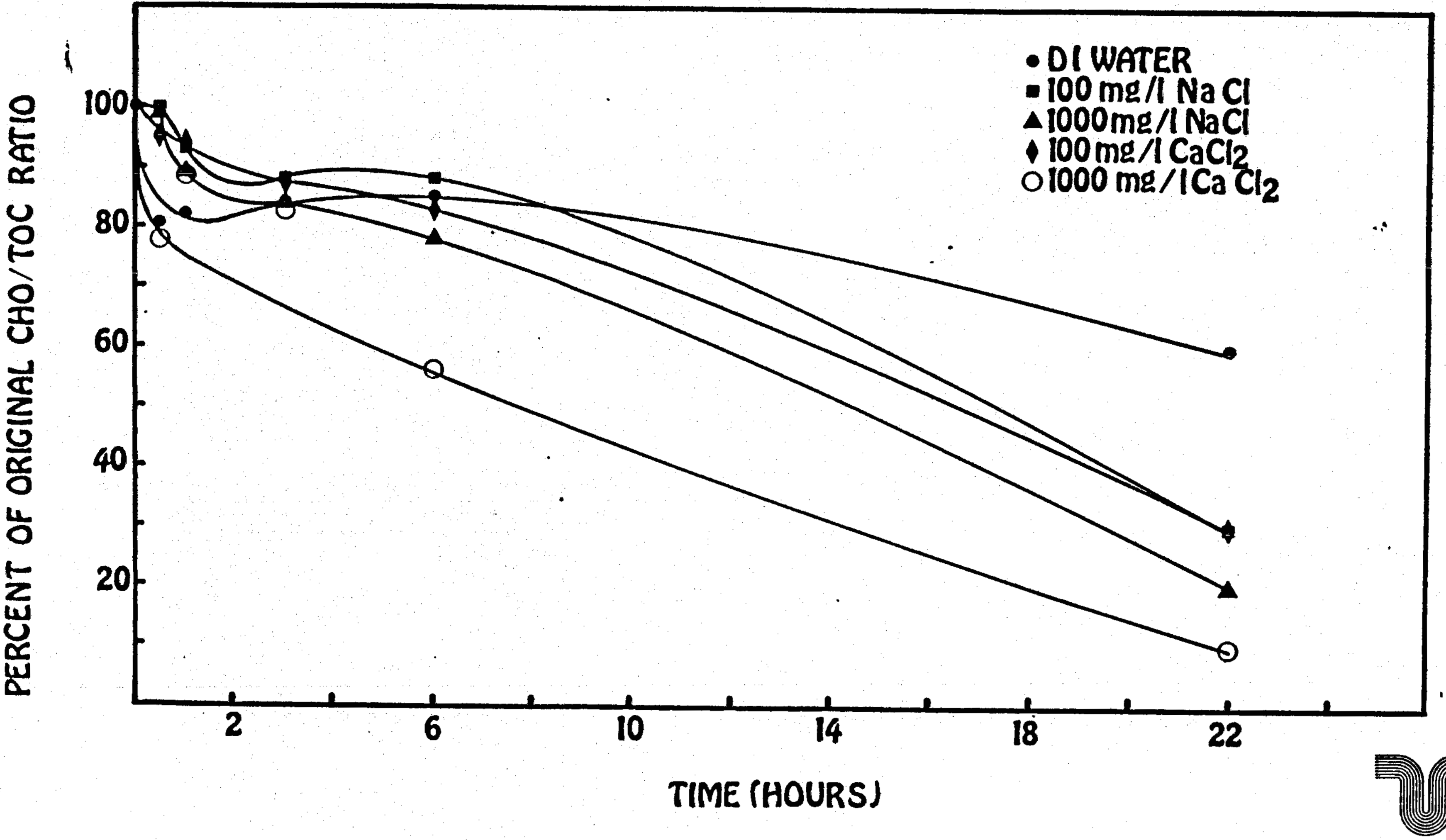


FIGURE 12

DEGRADATION OF HYDROXYETHYLCELLULOSE (HEC)
AT 250°C STATIC CONDITIONS

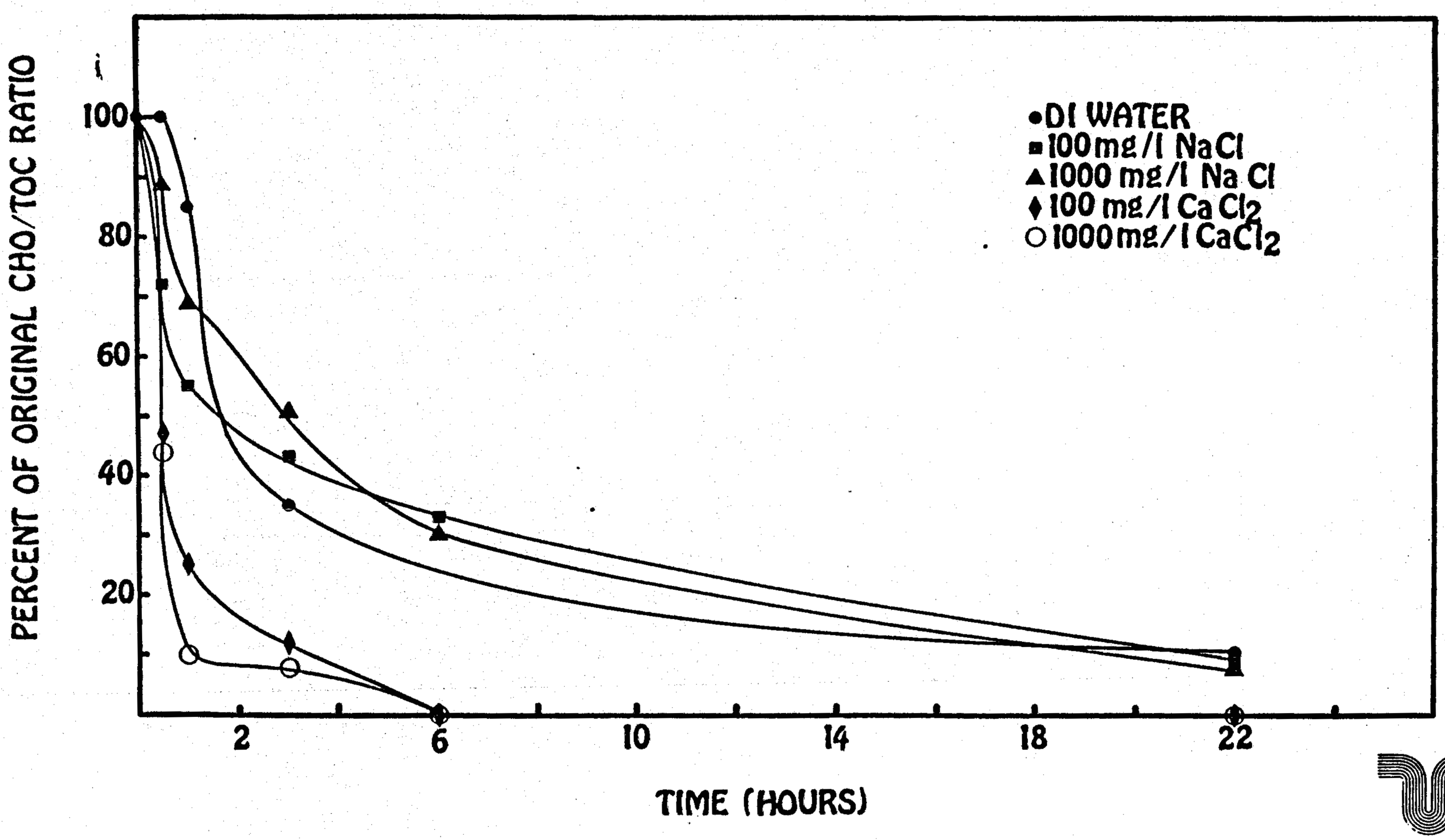


FIGURE 13

DEGRADATION OF XC POLYMER AT 150°C STATIC CONDITIONS

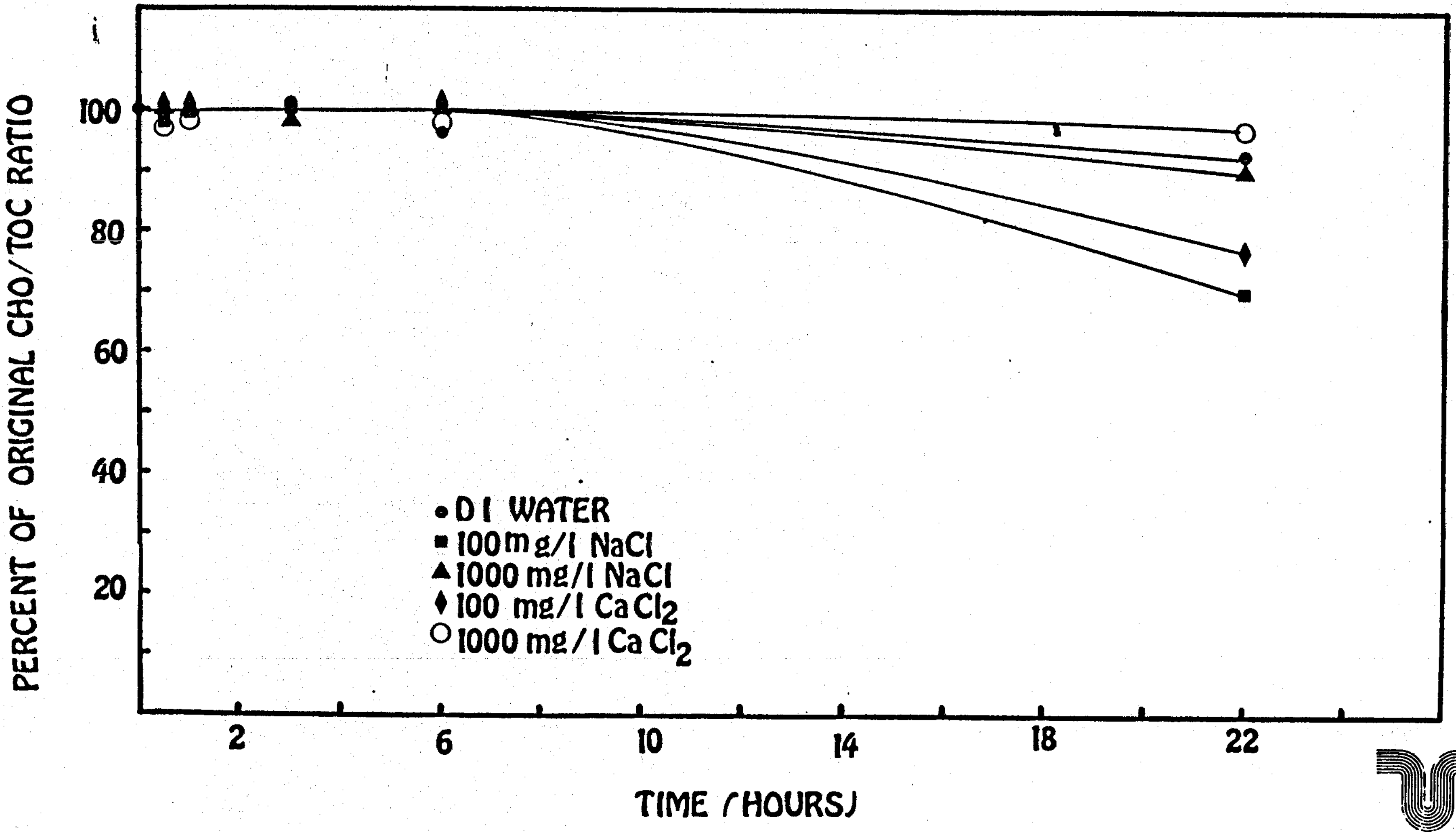


FIGURE 14

DEGRADATION OF XC POLYMER
AT 200°C STATIC CONDITIONS

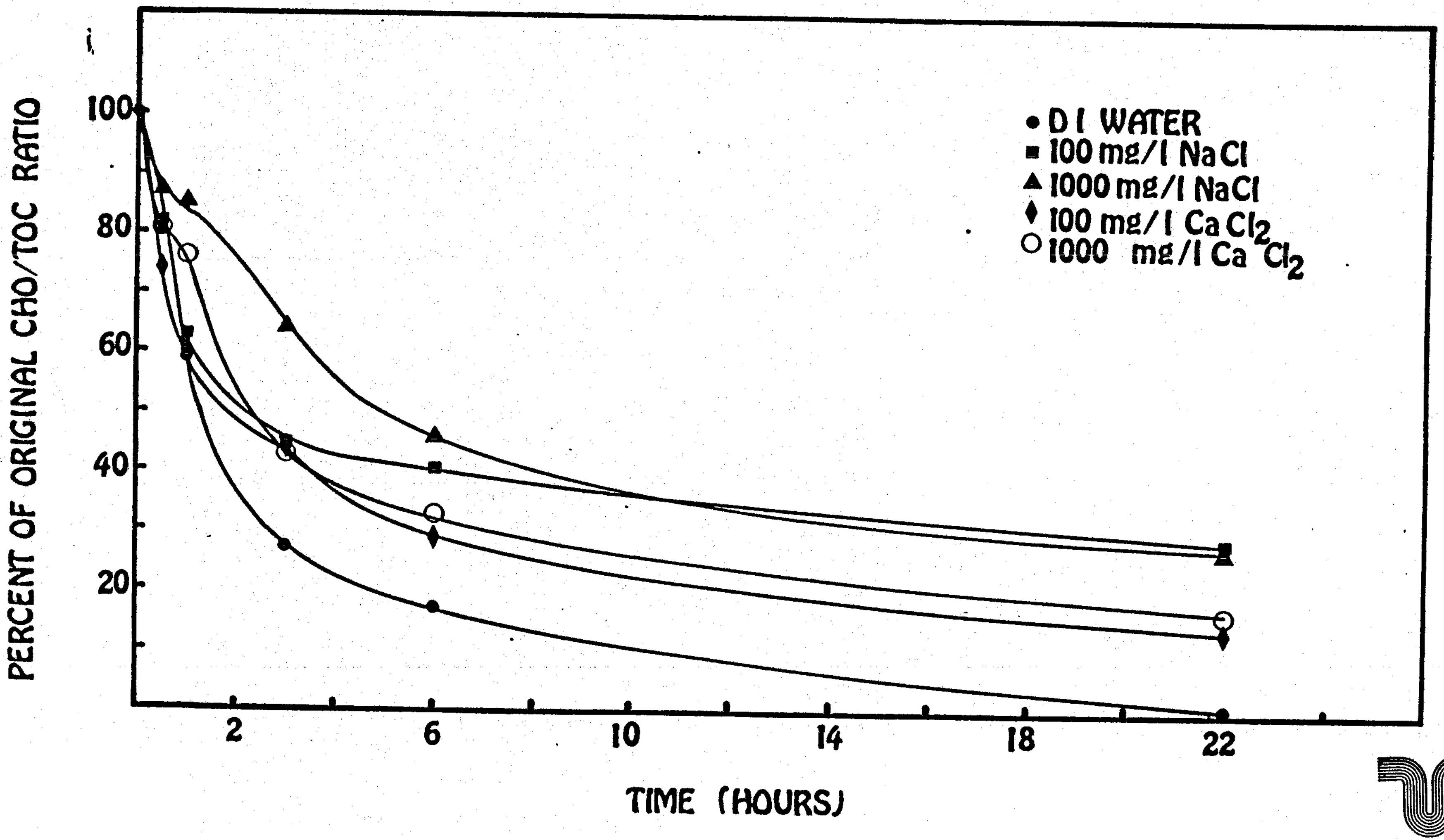


FIGURE 15

DEGRADATION OF XC POLYMER
AT 250°C STATIC CONDITIONS

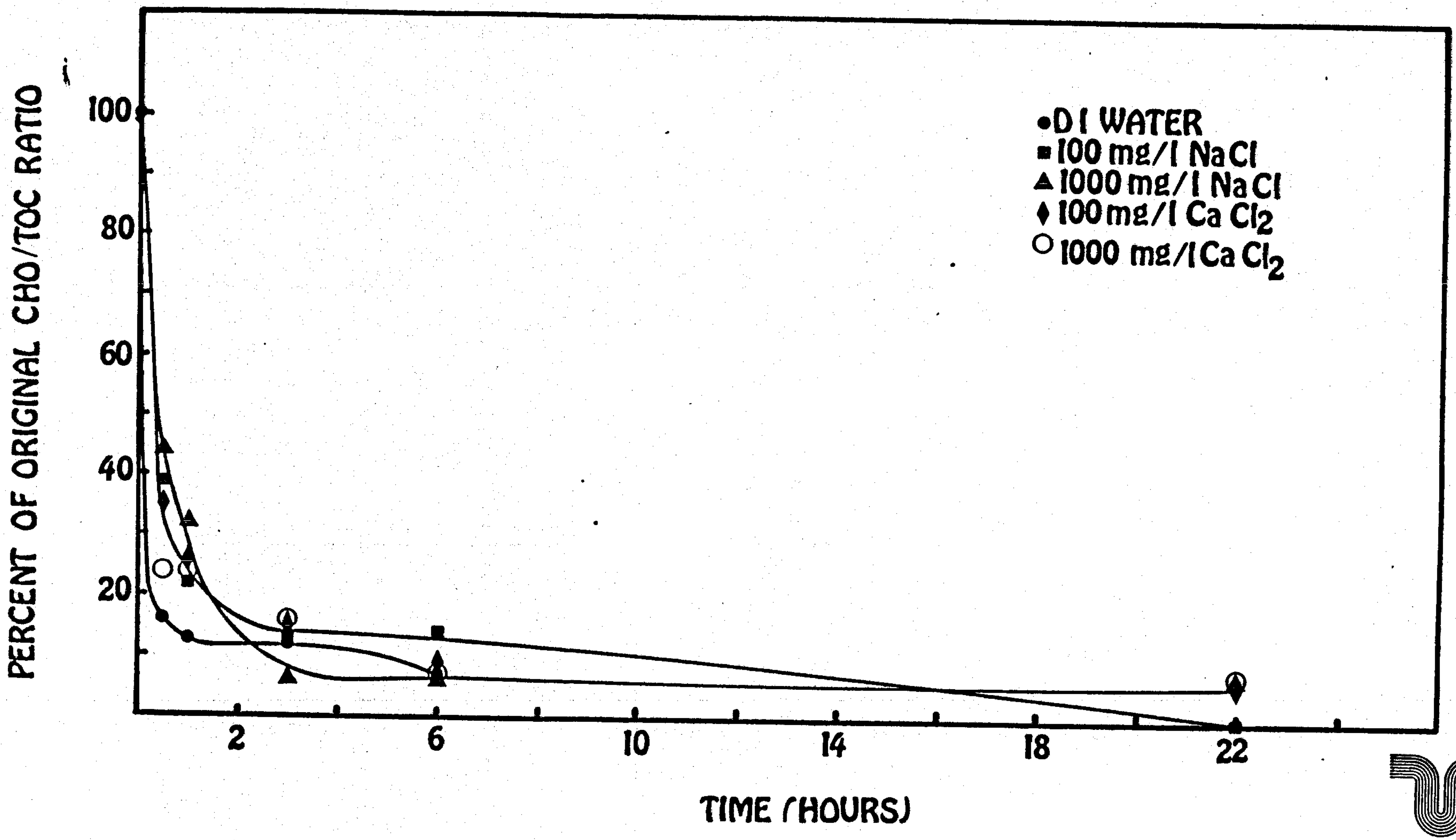


FIGURE 16

DEGRADATION OF HYDROXYPROPYLGUAR (HP GUAR) AT 150°C STATIC CONDITIONS

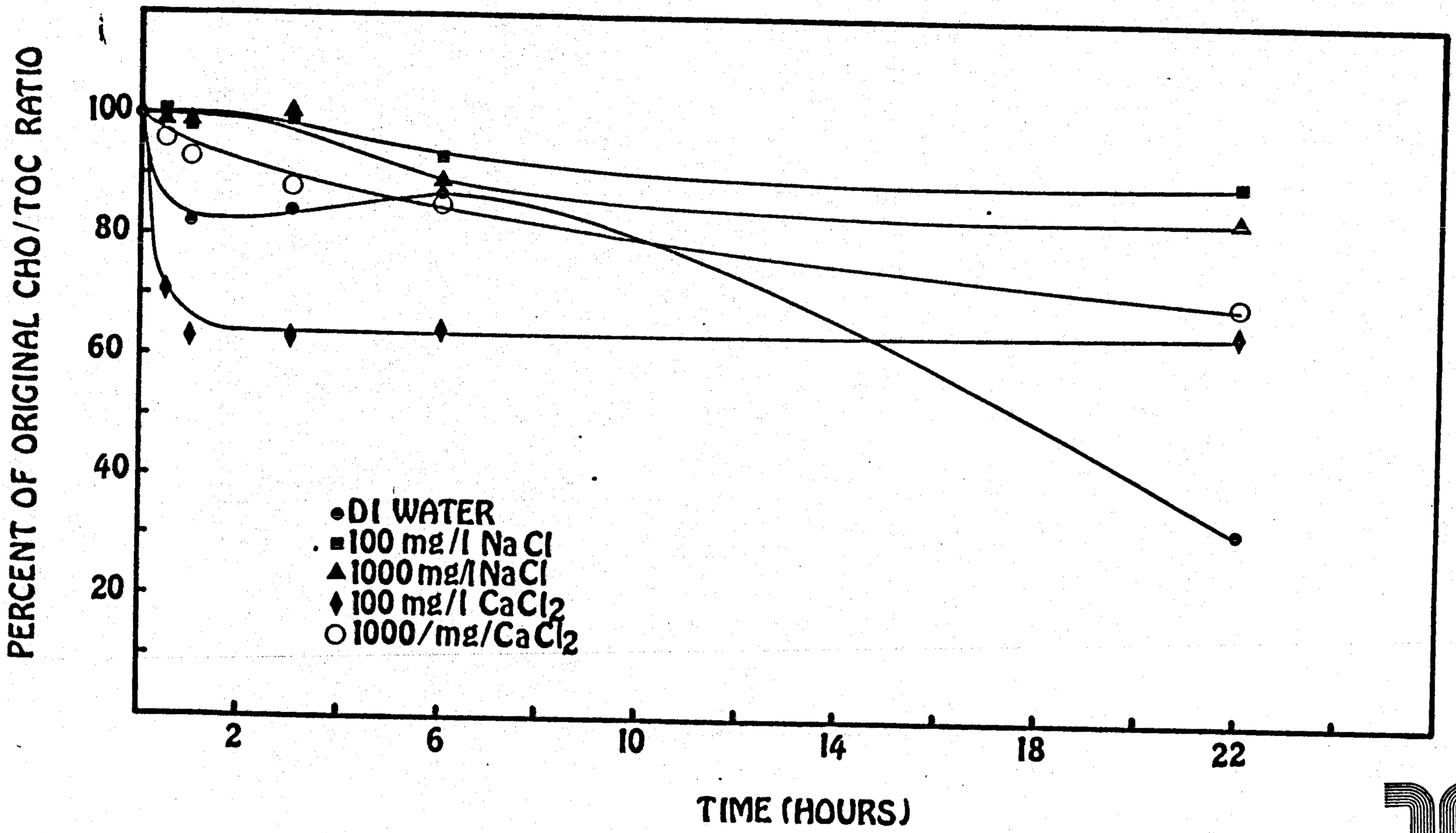


FIGURE 17

DEGRADATION OF HYDROXYPROPYLGUAR (HP GUAR) AT 200°C STATIC CONDITIONS

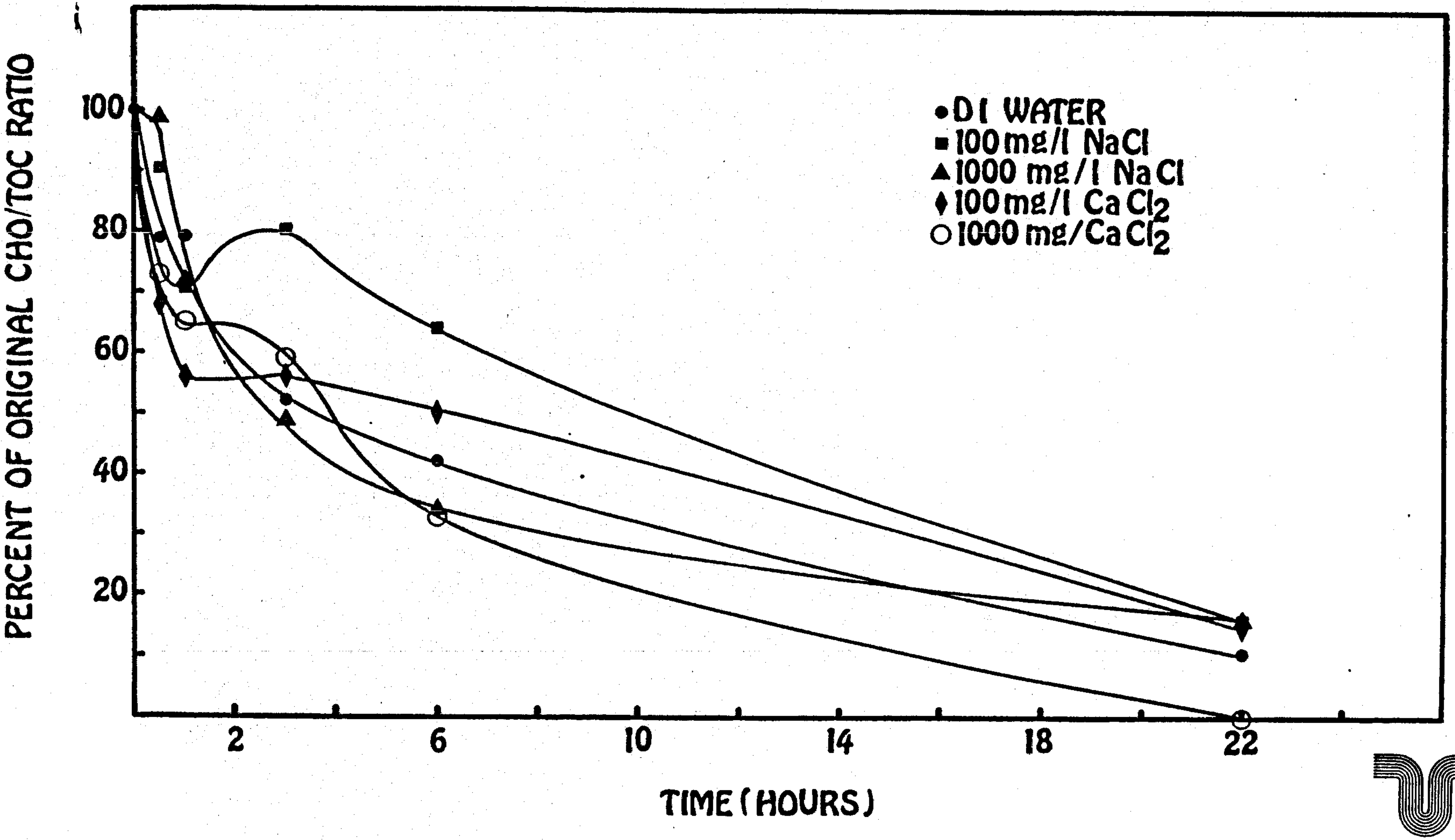


FIGURE 18

DEGRADATION OF HYDROXYPROPYLGUAR (HP GUAR) AT 250°C STATIC CONDITIONS

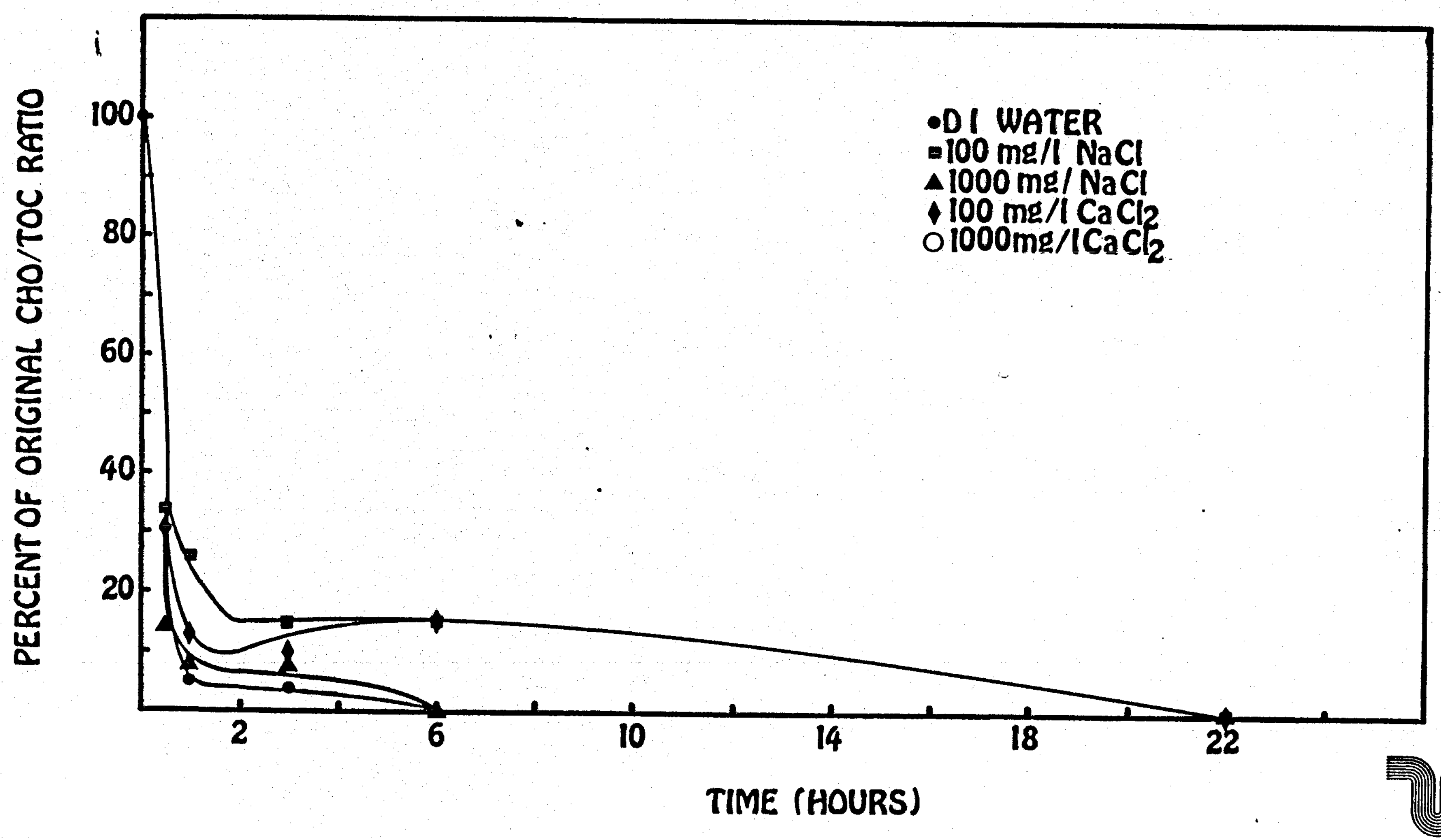


FIGURE 19

DEGRADATION OF COMMERCIAL FRAC FLUIDS
STATIC CONDITIONS
IN DEIONIZED WATER

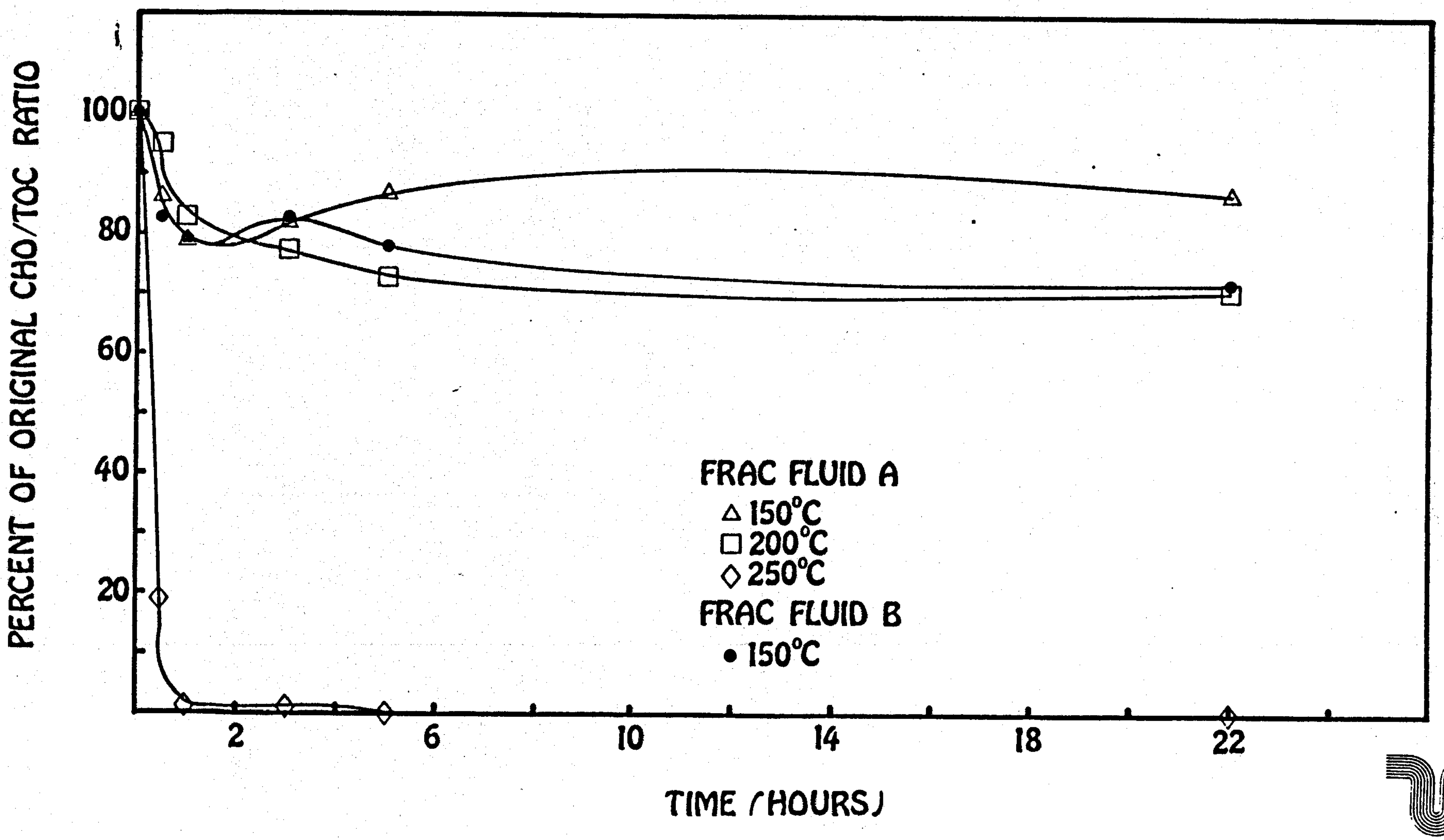


FIGURE 20

DEGRADATION OF CARBOXYMETHYLCELLULOSE (CMC)
DYNAMIC CONDITIONS
20/40 MESH SANDPACK
3000 mg/l TDS BRINE

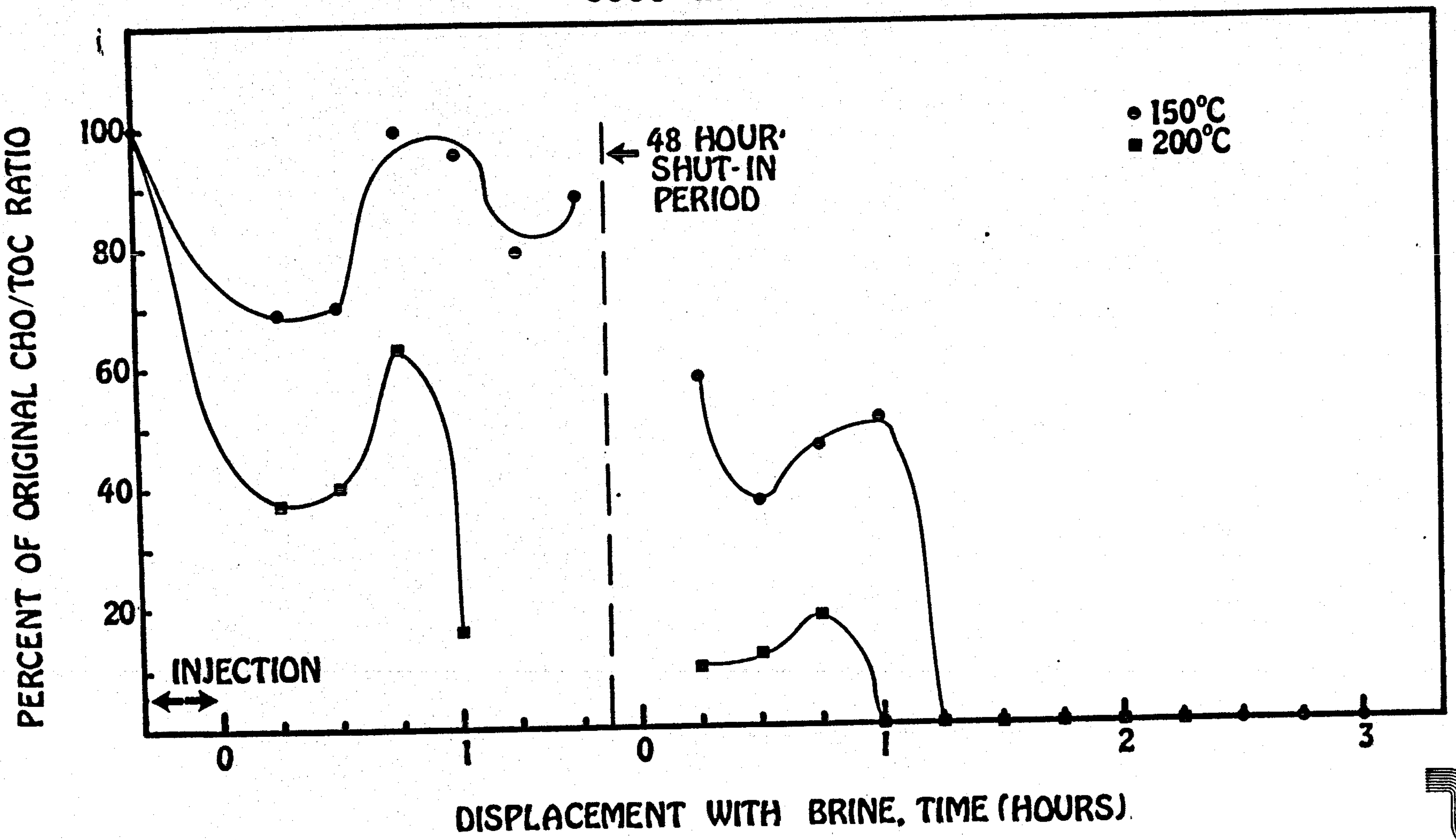


FIGURE 21

DEGRADATION OF HYDROXYETHYLCELLULOSE
DYNAMIC CONDITIONS
20/40 MESH SANDPACK
3000mg/l TDS BRINE

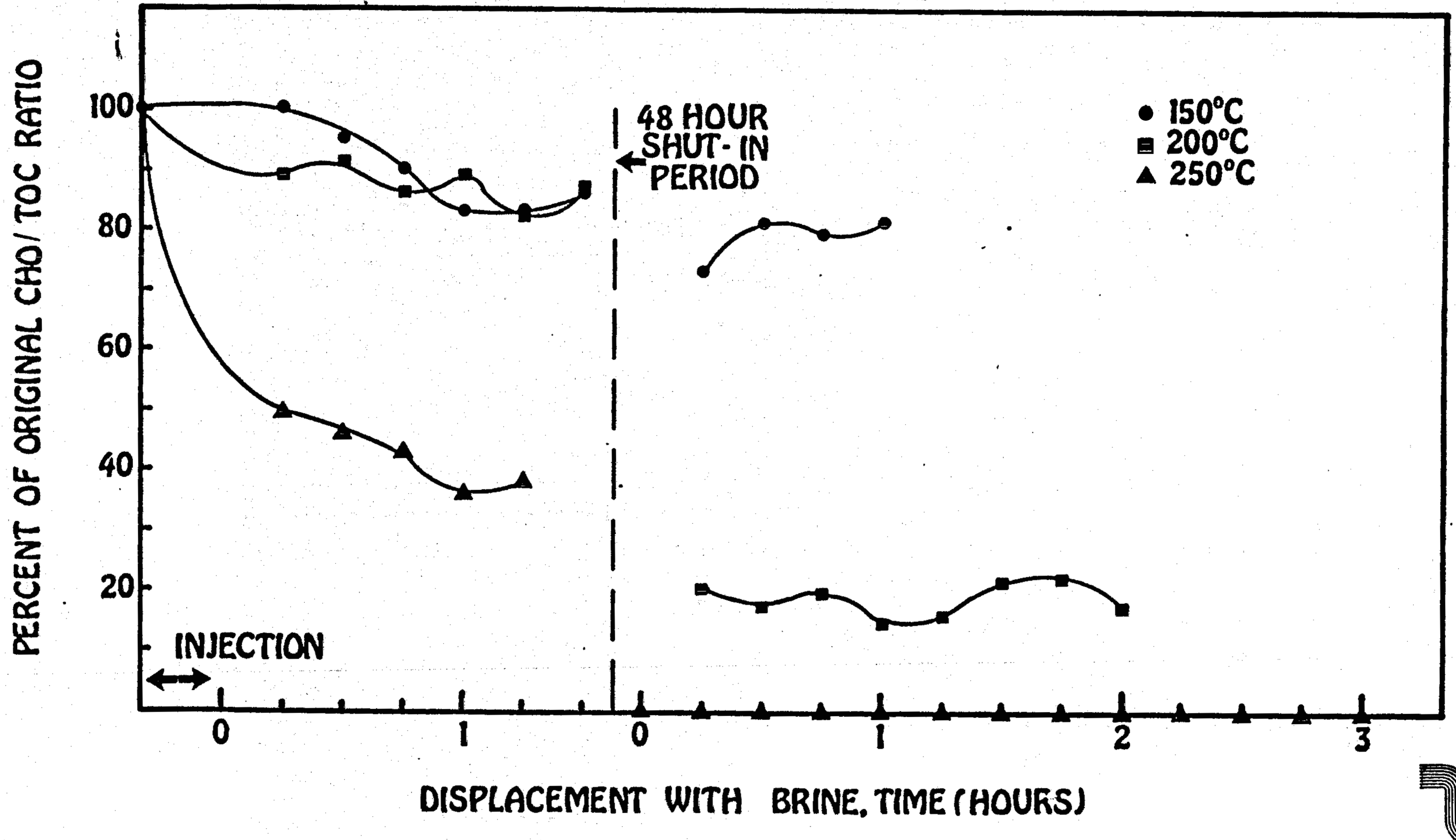


FIGURE 22

DEGRADATION OF XC POLYMER
DYNAMIC CONDITIONS
20/40 MESH SANDPACK
3000mg/l TDS BRINE

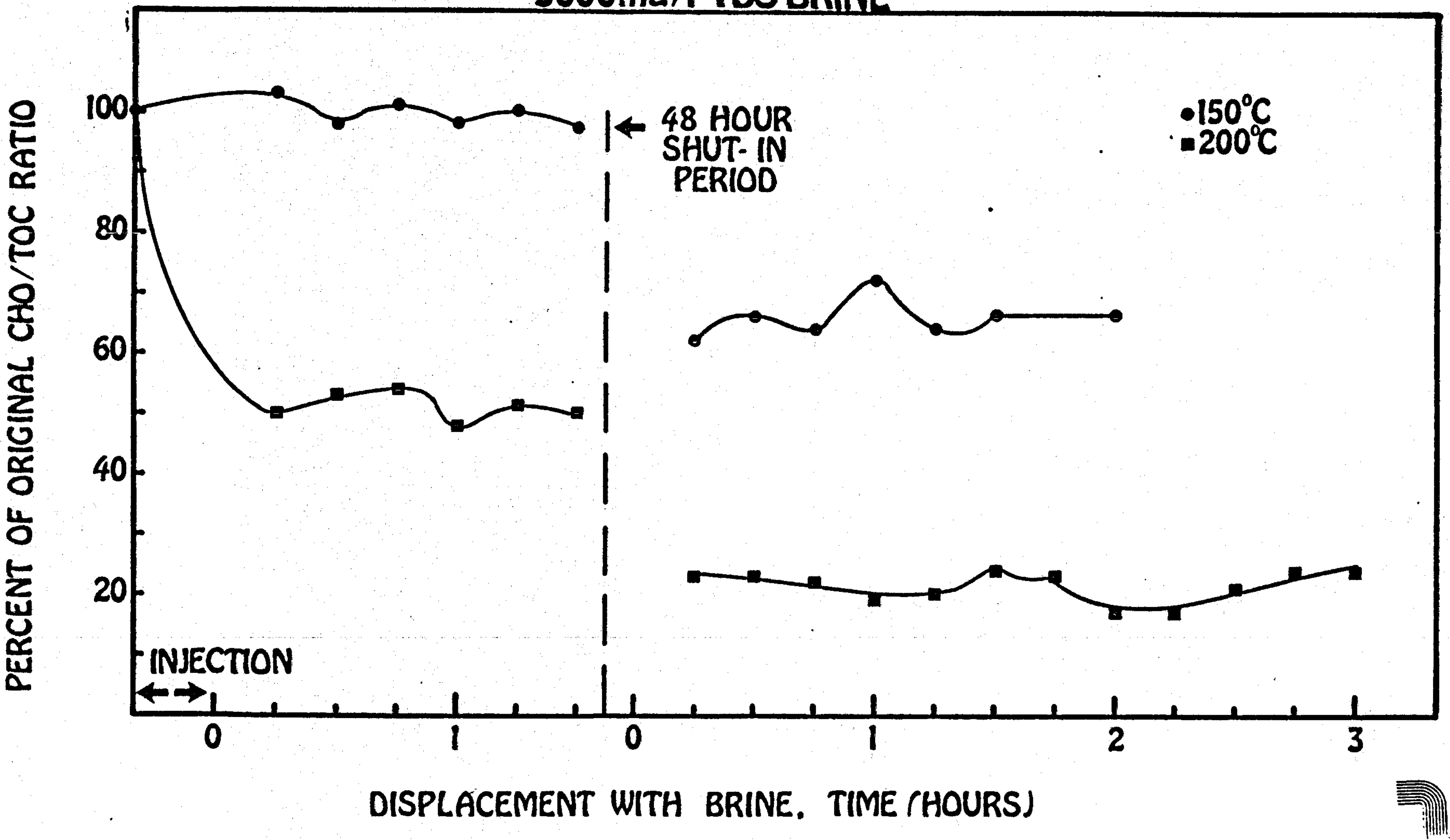


FIGURE 23

DEGRADATION OF HYDROXYPROPYLGUAR(H P GUAR)
DYNAMIC CONDITIONS
20/40 MESH SANDPACK
3000 mg/l TDS BRINE

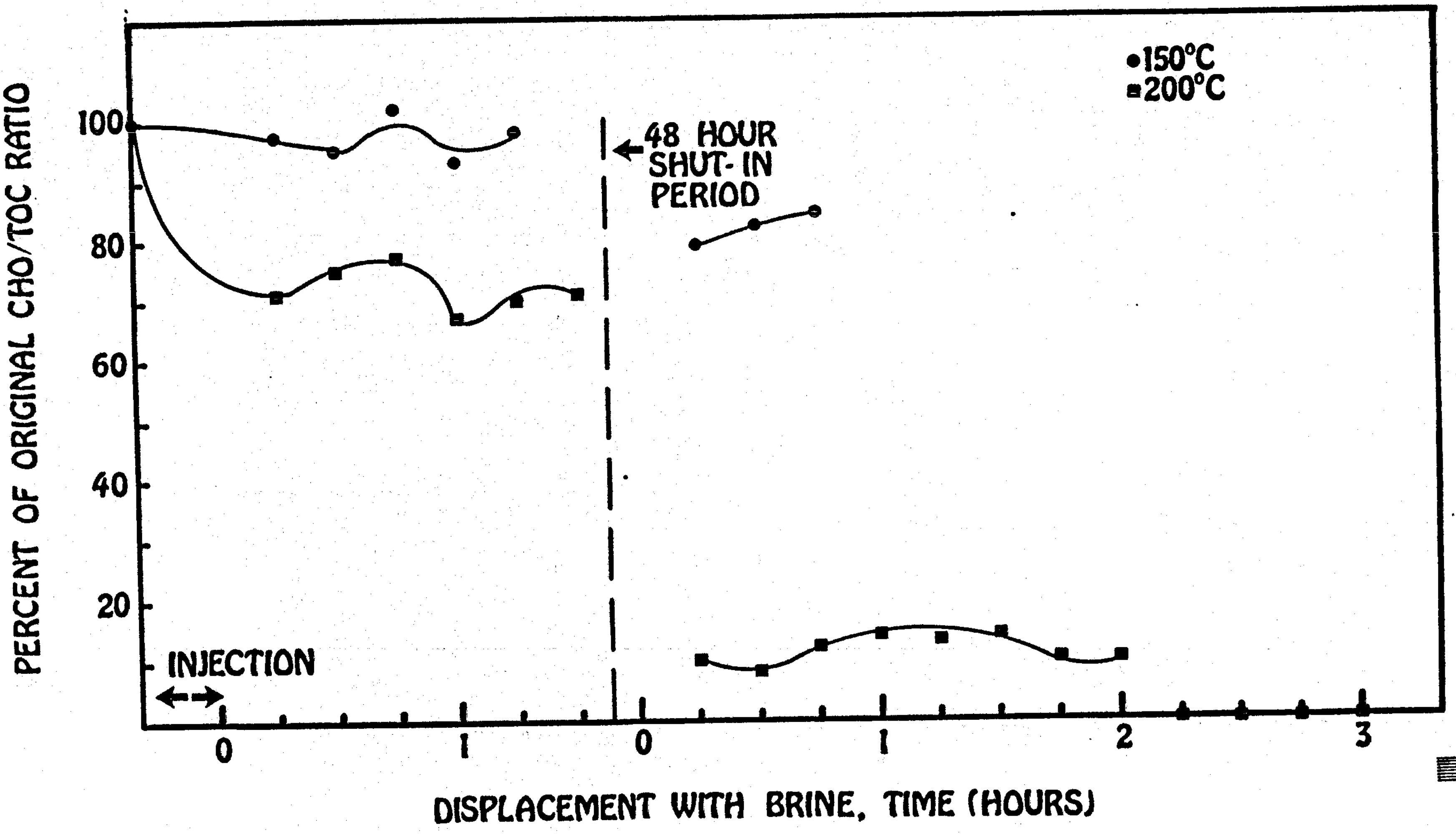


FIGURE 24

DEGRADATION OF FRAC FLUID A
DYNAMIC CONDITIONS
20/40 MESH SANDPACK
3000mg/l TDS BRINE

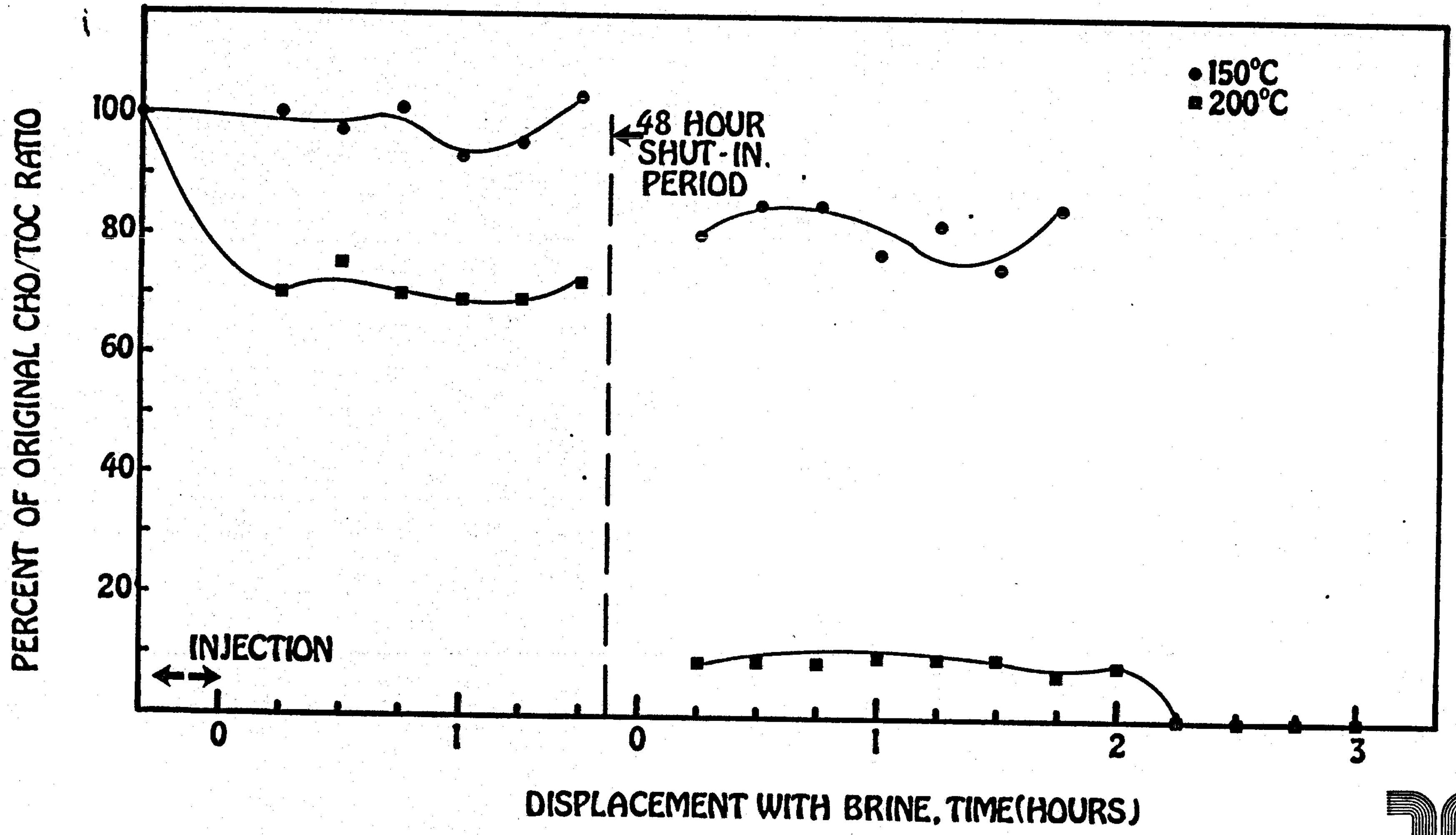


FIGURE 25

DEGRADATION OF FRAC FLUID B
DYNAMIC CONDITIONS
20/40 MESH SANDPACK
3000 mg/l TDS BRINE

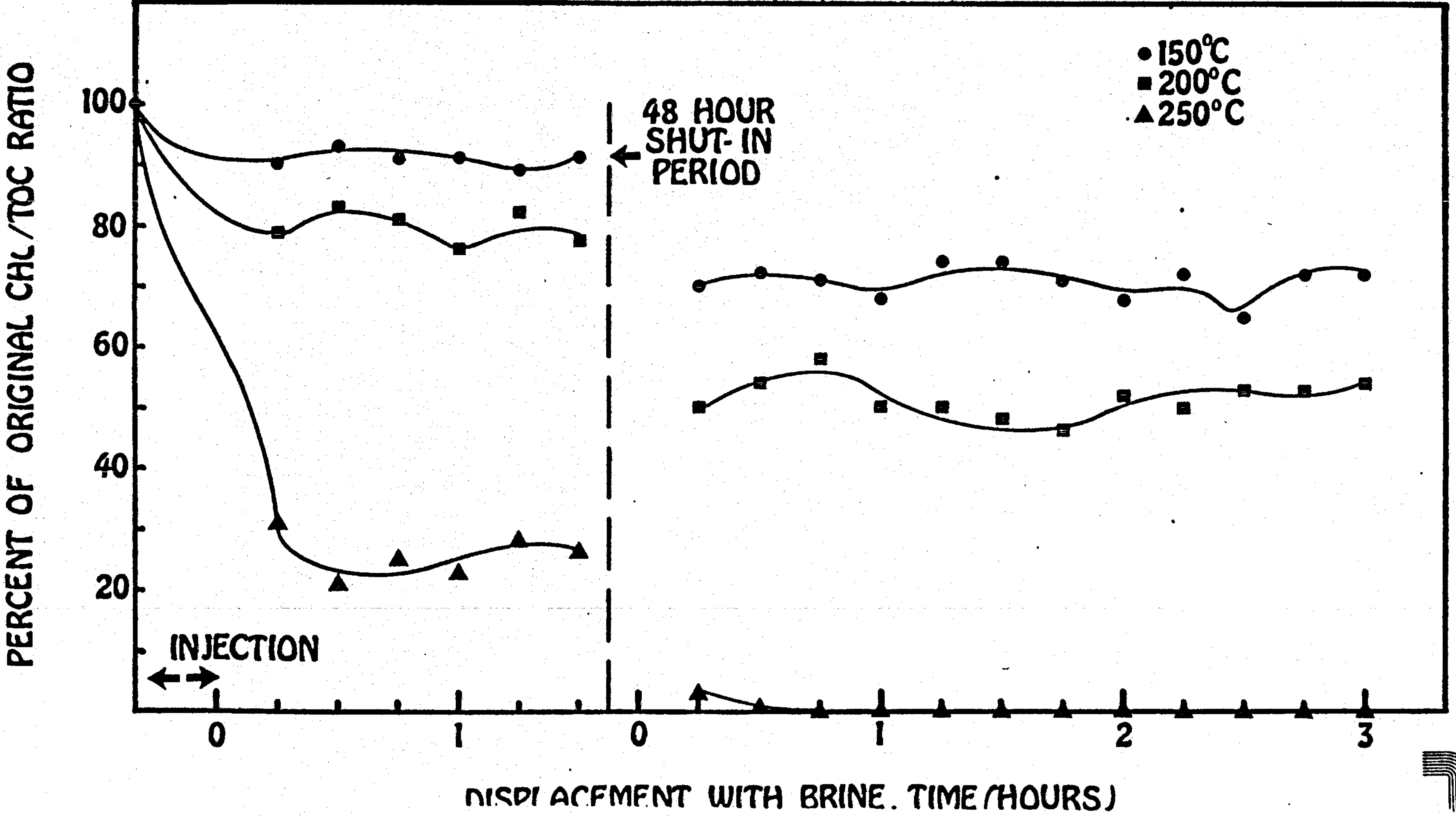
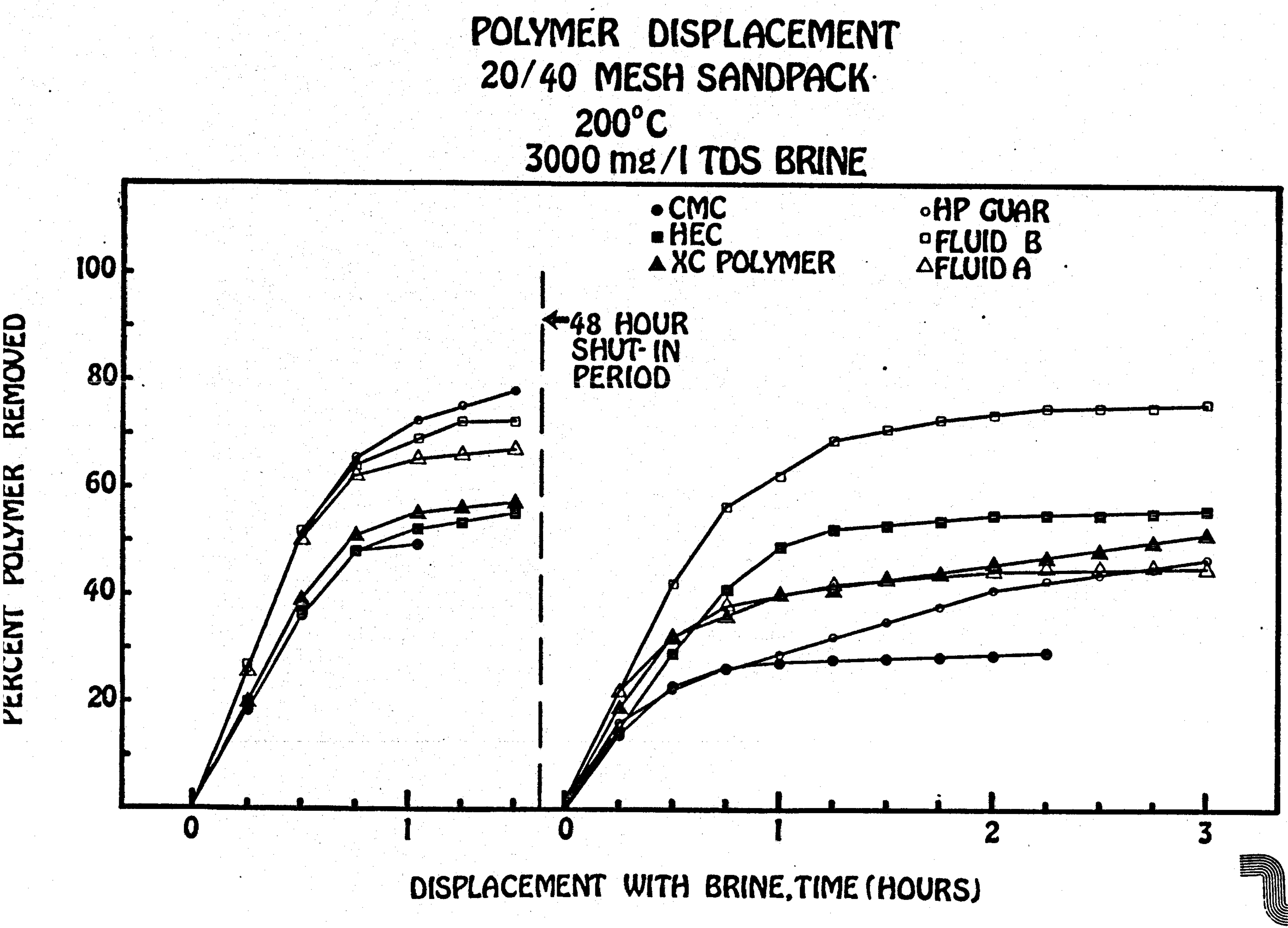
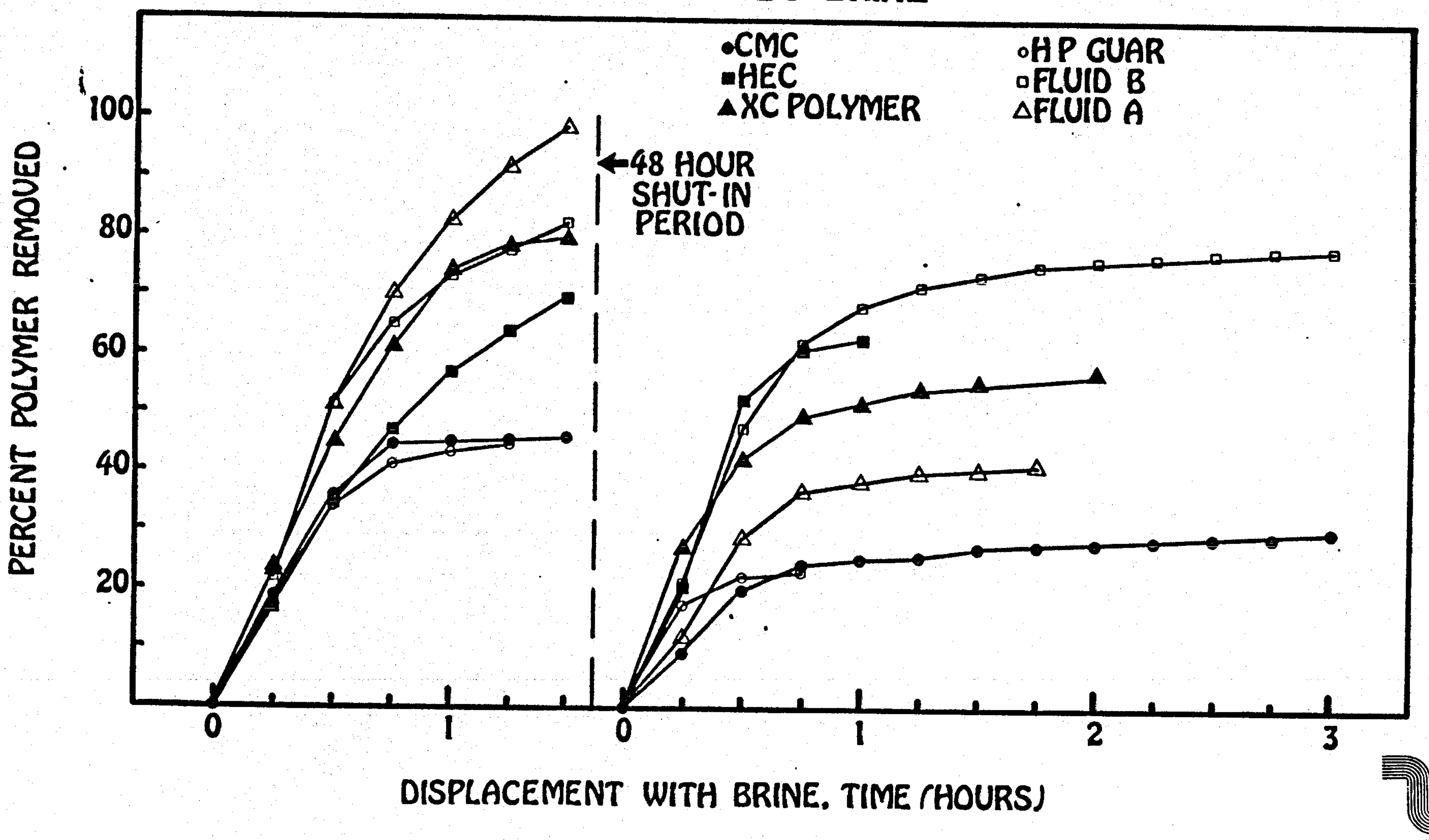


FIGURE 26



POLYMER DISPLACEMENT
20/40 MESH SANDPACK
200°C
3000 mg/l TDS BRINE
● CMC
■ HEC
▲ XC POLYMER
○ HP GUAR
□ FLUID B
△ FLUID A
← 48 HOUR SHUT-IN PERIOD
PERCENT POLYMER REMOVED
100
80
60
40
20
0
1
0
1
2
3
DISPLACEMENT WITH BRINE, TIME (HOURS)

FIGURE 27



POLYMER DISPLACEMENT
20/40 MESH SANDPACK
150°C
3000 mg/l TDS BRINE

APPENDIX A

HIGH PRESSURE LIQUID CHROMATOGRAPHY

1.0 INTRODUCTION

While the TOC and CHO data give information regarding gross chemical changes, no information is obtained as to subtle changes in the polymer. These changes are the ones most responsible for changes in fluid properties such as viscosity. However, techniques are not readily available to detect these subtle changes. Since this kind of information would be extremely valuable in unraveling the complex relationship between physical properties, chemical composition, and viscosity much effort has been put forth to develop some suitable analytical techniques.

Of the numerous methods considered, high pressure liquid chromatography (HPLC) is the most promising. HPLC is often used to uniquely characterize organic materials - particularly thermally sensitive and high molecular weight ones. However, little is known how this previous use can be related to the classes of polysaccharides commonly used as frac polymers especially when the complexities of the chemical composition of the make-up water and other additives are introduced.

1.1 PRELIMINARY WORK

Preliminary work following previously published procedures of polymer analysis has been of limited success in our laboratories. Numerous problems were encountered with column plugging and poor instrument sensitivity when solutions of either guar, HP guar, or XC polymer were injected for analysis. Many of these problems could be traced back to the column packing material being used and the interaction of the high molecular weight polymers with the packing. Much more reproducible data was obtained when column packings designed for high molecular weight materials were used. At present, we find columns packed with either microporous silica (LiChrosphere 4000) or a controlled porosity glass (Electro Nucleonic Inc) to give satisfactory separations. Of the several solvent combinations investigated as eluants, water was superior in all respects. The following is a discussion of the work done to characterize frac polymers changes by HPLC.

1.2 MOLECULAR WEIGHT STANDARDS ON SILICA

Polydextrans are high molecular weight sugar compounds having a predetermined average molecular weight. They are used as molecular weight standards and to evaluate columns for resolution and for calibration of molecular weight distribution patterns.

Aqueous solutions (0.5%=5000 ppm) of various molecular weights of polydextrans were made up and injected onto the leading column of a series of two LiChrosphere columns (SI 4000 and SI 1000). The solvent system was 100% water at 40°C. Detection was via a Schoeffel SF770 variable U.V. detector set at 190nm, and the flow rate was 1 ml/min. The chromatograms demonstrate an initial peak which appears to be an impurity present in all the polydextran standards. The molecular weights, areas, and retention times are as follows:

Dextrans on SI 4000 and SI 1000 in 100% water at 1 ml/min and 40°. The detector was set at 190 nm.

MOLE. WT. X 1000	RT	AREA
10	395	268,538
40	374	42,562
70	365	73,448
500	338	152,655
2000	308	262,660

At a flow rate of 0.5 ml/min., the retention time lengthened but there did not seem to be any significant increase in separation capabilities. The resolution is not markedly improved.

1.3 POLYMERS ON SILICA

After running the high molecular weight standards (Dextrans), samples of the polymers used in this degradation study were run. The following is a description of these tests.

1.3.1 GUAR GUM

The initial polysaccharide tested was guar gum. Aqueous solutions (1000 ppm) of guar gum were made up and injected on the leading column of a series of two LiChrosphere columns (SI 4000 and SI 1000). The solvent system was 100% water at 40°C. Detection was via the Schoeffel SF770 set at 200 nm. Heating the guar gum solution to 150°C for 5 hours and/or dissolution in KCl or NaCl aqueous solutions caused the chromatogram to shift indicating a lower molecular weight material.

1.3.2 XC POLYMER

Naturally occurring XC polymer was the next polysaccharide tested. Aqueous solutions (1000 ppm) of XC polymer were made up and checked under the same conditions as with guar gum. Exposure of XC gum to heat or salt solutions resulted in basically the same type of shift as with guar gum.

1.3.3 HYDROXYPROPYL GUAR

The third polysaccharide to be checked was HP guar. Aqueous solutions (1000 ppm) of hydroxypropyl guar gum were made up and examined chromatographically under the same conditions as for guar gum and XC polymer. The polymer was treated with heat and salt solutions, and the results were similar to that for guar gum or XC.

1.3.4 FRAC FLUID SYSTEMS

The last polysaccharide checked was a titanium cross-linked version of guar gum designated Frac Fluid A. The columns were immediately ruined with these solutions. As such, no consistent data is available for it.

1.3.5 SUMMARY OF WORK WITH SILICA COLUMNS

Problems were encountered with the silica columns going bad in relatively short periods of time, necessitating either repacking an old column or using a new commercially packed one, and recalibrating by checking retention times with Dextrans. Consistent and satisfactory data has been difficult to obtain on these studies. Silica packed columns (SI4000, SI1000 in series) achieve good resolution with polydextrans and polymer solutions. However, silica does adsorb cations to a great degree and no reliable method for cleaning the column packing has been found. The life of silica packed columns has been very short in the testing with polymer solutions containing any salts, especially samples from the field, which are always combined with heavy brines.

1.4 CONTROLLED PORE GLASS COLUMNS

In exploring different types of packing material, it was found that controlled pore glass (CPG) provides good separation for polydextrans and polymers comparable to the silica packing. This packing material will also adsorb cations but can be cleaned up with a 20% nitric acid wash, and also can be packed with a higher success rate than with silica.

Polydextrans in an aqueous solution (0.5%) were run through controlled pore glass (CPG) packed columns in series, (CPG 2000 followed by CPG 500). The detection was via the U.V. SF770 set at 200 nm and an LDC refractive index detector set at midrange attenuation. The peaks were eluted with the mobile phase of 100% water at 2 ml/min. Retention times were reproducible:

Dextrans (0.5%) on CPG 2000 and CPG 500 in 100% water at 2.0 ml/min SF770 at 200 nm and R.I. at midrange attenuation.

MOLE. WT. X 1000	RT	AREA
10	229	19,418
40	224	19,840
70	219	19,800
500	199	19,774
2000	194	16,657

In order to check the separation capability of the CPG 500 column, this column was used alone and the full series of dextrans injected onto it. Elution was by 100% water. The CPG 500 packing has a pore volume of 0.8 ml/g and a large molecular weight operating range (70 to 10,000 x 1000). The retention times were reproducible but peak areas not as consistent as with the 2000 and 500 combination. The retention times are as follows:

Dextrans on CPG 500 in 100% water at 2.0 ml/min SF770 at 200 nm and R.I. at midrange attenuation.

MOLE. WT. X 1000	RT	AREA
10	124	25,000
40	119	26,000
70	114	29,000
500	99	19,000

1.4.1 POLYMERS ON CONTROLLED PORE GLASS

A major problem encountered during the study is the inability to obtain consistent polymer chromatograms in the presence of salt. Cationic absoption on silica shortens the life of the column, and protective coatings were considered to alleviate this. Coatings such as carbowax, and sodium dodecylsulfate, which prevent ion absorbtion, also absorb in the same U.V. range as the polymers (190-200 nm). A Refracto Monitor refractive index detector was installed to provide a second means of detection for polymers in the presence of coatings and buffers. Controlled pore glass packing was chosen as the suitable stationery phase.

1.4.2 PRELIMINARY STUDIES WITH XC POLYMER AND GUAR GUM ON CPG

XC Polymer and guar gum were analyzed on controlled pore glass (CPG) packed columns. Aqueous solutions (0.25% by wt/vol) of guar gum were injected on the leading column of two CPG columns (CPG 2000 and CPG 500). The solvent system was 100% water at 40°C. Detection was via the Schoeffel SF770 variable U.V. at 200 nm on channel 2, and the Refracto Monitor Model 1107 refractive index detector on channel 1. The flow rate was 2.0 ml/min. There is a marked difference in sensitivity at this concentration, as the U.V. response is much more sensitive.

In setting detection limits, it was found that the R.I. and the U.V. is sensitive to 0.05% (500 ppm) or less polymer, while the R.I. is only sensitive to 0.25% (2500 ppm). This presented a problem in that the routine degradation samples were in the 500 ppm or less range.

Aqueous solutions (0.25% by wt/vol) of XC polymer were made under the same conditions as guar gum and similar sensitivites with both detectors were found. These solutions (deionized water) were heated for various lengths of time and samples analyzed by HPLC. Figure 1 of the Appendix illustrates qualitative differences in the chromtograms. Most noticeable is the disappearance of the component eluting at short retention times (i.e., "0" hr. sample) and the appearance of a component eluting with longer retention time (i.,e. "22" hr. sample).

As discussed above, changes in retention on this particular column packing material are known to be related to molecular weight with lower molecular weight polysaccharide fragments having longer retention times. Unfortunately, when the XC polymer was made up in a calcium chloride solution, peaks were observed in the chromatogram with rentention times similar to those of the polymer which had been heated in deionized water only. This is illustrated in Figure 2 of the Appendix where chromatograms of a 0.25% solution of XC polymer in 0,300,800 and 5000 ppm calcium chloride solutions are shown. Note that the "short retention time" peak (i.e. initial polymer) is present in all solutions and that the "long retention time" peak increases non-linearly with calcium chloride concentration. These salt solutions when heated caused an increase in intensity of the "long retention time" peak as would be expected from the results in deionized water. Unfortunately, the peaks for the degradation products could not be resolved from those present in the original calcium chloride solution before heating.

After several HPLC runs with polymer and high salt concentrations, cation adsorption on the CPG columns was evident by an elevated pressure and successively longer retention times for identical samples. The columns were then flushed with water until neutral to pH paper. The same conditions as previous runs were set and samples run again. The chromatograph showed no impairment to the columns, and did achieve a 200 psi reduction in pressure drop across the column.

The relatively rapid degradation of CPG column performance suggests it will not prove any better than the silica packing in resistance to cation absorption and subsequent column degradation, although the CPG columns can be recovered with 20% nitric acid, as already mentioned. Unfortunately, coating the columns with sodium dodecylsulfate, carbowax, or buffering the solvent system with 0.05 m sodium acetate to prevent absorption is not really possible since these compounds adsorb in the U.V. range used (190-200 nm) and the R.I.'s sensitivity is too low to allow dependence upon it alone.

These problems have led to the conclusion that the use of the R.I. (with column coating) and silica packing (with its irreversible degradation) is not feasible in this study. Therefore, further experimentation was confined to CPG packing material, the U.V. detector, and polymer samples in deionized water.

2.0 COLUMN PACKING

In order to be able to have a supply of fresh columns, attempts were made to pack columns, using a variety of pore sizes and material types. A Micromeritics slurry packer Model 705 was used and a slurry made consisting of 2.5 gram packing material in 10 ml of 1:1 mixture of chloroform:methanol. The packer reservoir was placed in a Bransonic sonic oscillator for 45-60 minutes. Then while being stirred, the slurry was forced into a 25 cm stainless steel column (ID 4.2 mm) with a constant pressure Haskell Model MCP-71 pneumatic pump at a pressure of 5000 psi. The pressure was maintained for 20-30 minutes. The flow rate was initially at 20 ml/min and eventually slowed to less than 1 ml/min. The pressure was allowed to bleed off by shutting off the air supply.

Column evaluation was done with the dextrans and polystryrenes. The LiChrosphere columns were checked by comparison with commercially packed columns.

Comparing experimentally packed silica SI 100 and commercial SI 100 (LiChrosphere), using 100% Tetrahydrofuran (THF) as the mobile phase, and the SF770 U.V. detector set at 190 nm, polystyrenes in the THF (0.5%) eluted at similar retention times for both the commercially packed and experimentally packed column. Also, dextrans in aqueous solution (0.5%) and 100% water as the mobile phase, when injected on either column, demonstrated similar retention times and separations. This was used as evidence for a well packed column.

The CPG columns are not commercially packed, and so a comparison is not possible. The only criteria used to date is the consistency of peak retention of dextrans.

3.0 ANION AND CATION INTERFERENCE

Silica and controlled pore glass packing both demonstrate adsorption when exposed to cation concentrations. When using salt solutions, chromatographs were not consistent over a period greater than 5 runs. Injection of potassium/water solutions, at a flow rate of 0.5 ml/min showed a strong peak in the vicinity of 689 seconds, but did not stay constant for long. The chloride peak would gradually shift to increasingly longer retention times, indicative of increasing column adsorption. Adsorption of sodium, calcium, magnesium, and potassium results in longer retention times, increased column pressure, and subsequntly shortened column life.

As was previously mentioned, the CPG columns can be recovered by washing with 20% nitric acid/water. However, all attempts to recover the LiChrosphere columns met with failure. The attempts included prolonged flushing with water and methanol. Sodium chloride (1.0 normal) was also used, as the sodium cation is reportedly removable with prolonged flushing with water, and might have been expected to displace any other cation.

However, an additional problem encountered is that chloride and nitrate show strong peaks (by both U.V. and R.I.) with retention times similar to the various polymers on the columns now being used. At the moment, smaller pore size packing material is being considered in order to alter the retention times of polymer and nitrate.

4.0 DETECTORS

The Schoeffel SF770 variable wavelength U.V. detector is very useful for the analysis of ultraviolet absorbing solutes. It is capable of very high sensitivity, is relatively insensitive to mobile phase flow and temperature changes, very reliable, has a gradient elution capability, but has a widely varying response for different solutes. For the analysis of dextrans and polymers in aqueous solutions, the U.V. response is sensitive and reproducible. The problems encountered with its use with polymers arises from column and adsorption inhibitors absorbing at the same wavelength. The sensitivity appears to be strong with dextrans, polymers, and polystyrenes.

A problem arising from the strong sensitivity of the U.V. detector is that contamination in water solutions from plastic containers can be detected when checking for low concentrations at polysaccharides at low attenuation settings. Because of this, samples and solvents were stored in glass only, and deionized water taken directly from the water still.

The LCD Refracto Monitor monitors differences in refractive index between a pure references mobile phase and a column effluent. The refractometer is very versatile, but has moderate sensitivity for solutes. It is sensitive to temperature changes and difficult to use with gradient elution. As with the U.V. detector, it is not sensitive to mobile phase flow changes. The problems encountered are due to the lack of sensitivity to various solutes.

FIGURE 1

THERMAL DEGRADATION OF POLYMER AT 150°C IN DEIONIZED WATER

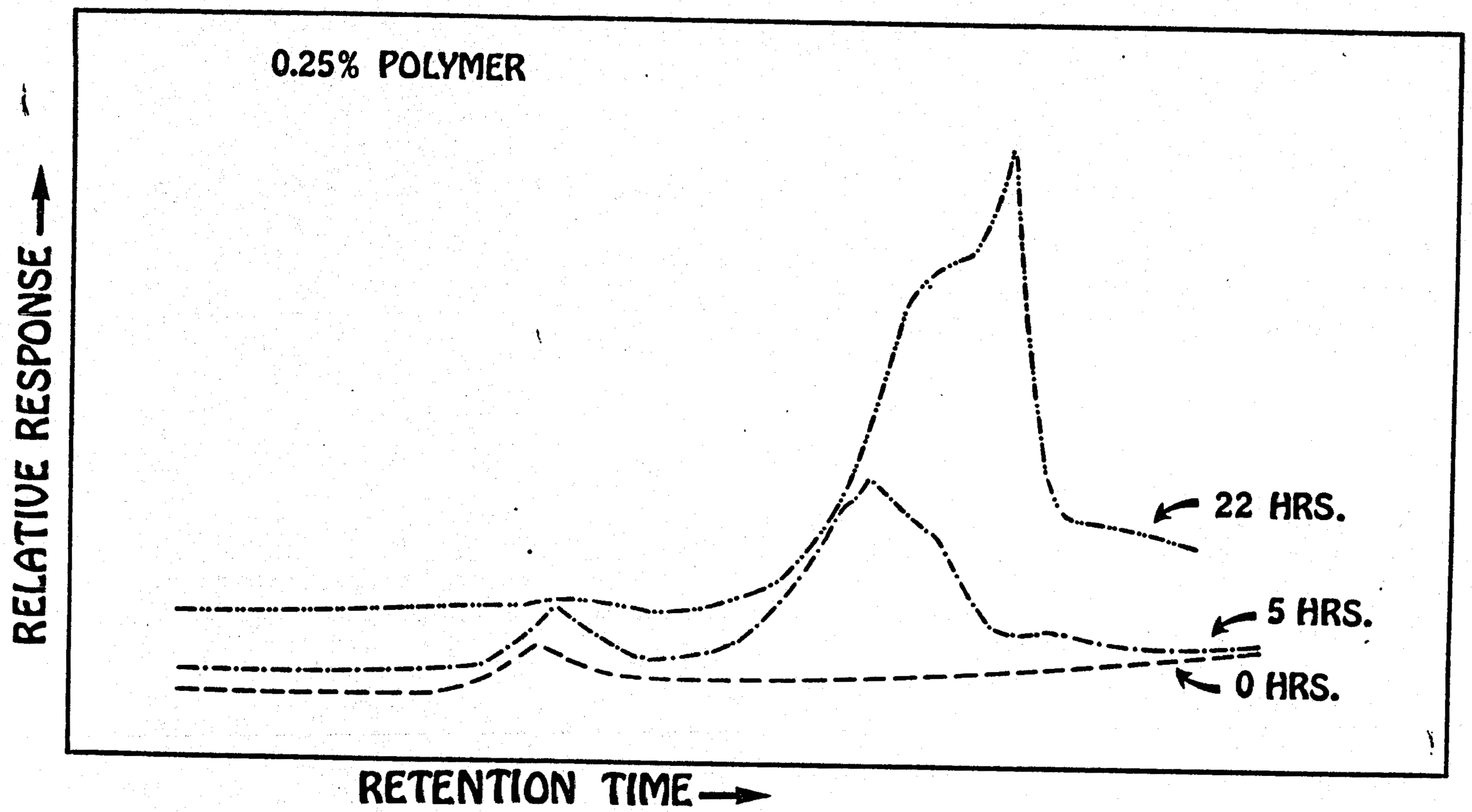


FIGURE 2

HPLC PROFILE OF XC POLYMER IN VARIOUS CONCENTRATIONS OF CALCIUM CHLORIDE