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Late Results of a Polymer Pilot Test: Performance, Simulation Adsorption, and Xanthan Stability in the Reservoir

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ABSTRACT

A polymer flood pilot project had been performed in the Eddesse-Nord sandstone reservoir (Germany) with a depth of 350 m, a temperature of 22 °C, an average permeability of about $1 \mu\text{m}^2$, and a thickness of 5 m. The clay content in the sandstone was about 10 %.

A xanthan-solution with a concentration of 800 ppm was injected from 1985 until 1988 into 2 wells. The xanthan was provided as a 2 % fermentation broth.

In mixing of the polymer and during injection of the polymer solution no severe problems were encountered. There was no plugging tendency in the wells observed, which is attributed to a thorough laboratory quality testing.

A response in the production wells occurred earlier than predicted by reservoir simulation and the incremental oil production was somewhat higher than the predicted 6 % of the original oil in place.

Several simulation studies have been performed using 2 different numerical simulation models. Good history matches could be obtained with respect to production performance during the water flood phase and flow of tracers in the reservoir. The different salinities of the injected and the original reservoir water were used as tracers, as well as the polymer and the formaldehyde, which was used as biocide.

Polymer was produced in significant amounts in one well. The produced xanthan as well as the xanthan that was

injected were analysed for molecular weight, chemical composition, and solution properties. The xanthan molecules were also examined by electron microscopy.

The polymer project can be regarded as successful in terms of injection and production performance. Reservoir simulation results as well as laboratory studies have shown an adsorption of xanthan of 30-40 $\mu\text{g/g}$. The xanthan produced in one well, after it had been in the reservoir for about three years, showed no degradation, neither chemical nor bacterial.

INTRODUCTION

The situation in the oil fields operated by Preussag is characterised by increasing water cuts, which have already reached an average value of about 80 % and in some cases up to 97 %, which is close to the economic limit. This is why Enhanced Oil Recovery is of major concern for these oil fields.

Besides steam flooding, which is being applied in several fields with heavy oils, surfactant flooding and polymer flooding are expected to be the most suitable EOR method for many of these oil fields. As polymer flooding is the only chemical method, that is technically and also economically feasible, a polymer pilot project was started in 1984 in the small oil field Eddesse-Nord. The reservoir is shallow with depths between 150 to 350 m, which is favourable for drilling and workover, but a constraint for injection pressure, especially during polymer injection. Furthermore the temperature is very low at 22 °C, which may lead to high adsorption of chemicals and high levels of bacterial activity. The relatively high clay content of about 10 % was also not very favourable.

References and illustrations at end of paper

Though these are very harsh conditions for a polymer flood it was decided to start a small pilot, because on the other side this was a possibility to study all of the effects in a real field case, which were found to be detrimental to chemical flooding in previous laboratory studies.

This paper deals mainly with the results of investigations on the chemicals produced from the reservoir.

RESERVOIR DESCRIPTION

The small block chosen for the pilot project is shown in Fig. 1. This block is separated from the rest of the field by 2 sealing faults. A total of nine wells had been drilled in this block, so the structure was fairly well known. Five of these nine wells were still open and could be used for the polymer project.

The reservoir may be divided into several different layers from which layer M was chosen for the pilot project. A log of well 96 is shown in Fig. 2. The reservoir data are summarised in Table 1.

All the wells drilled originally in this block were producing from different layers. Therefore in primary and secondary operations oil was produced only from well 90, which was because of the down dip position of this well not being optimal. Water was injected for only a short time into well 91 to maintain the reservoir pressure. During primary production the pressure then fell below the bubble point (2.00 MPa) and a secondary gas cap developed in the up dip part of the structure. Although well 90 is located near the oil water contact production was at water cuts of 50 - 70 % at low rates for a long period. Cumulative production in 1984 was 7085 m³ tank oil or 35 % of the original oil in place.

Well 96 was drilled in the up dip part of the reservoir before the polymer flood was started. The well was entirely cored in the reservoir zones in order to get fresh and representative core material for laboratory investigations.

POLYMER INJECTION

Before polymer injection was started a water preflush of 10 300 m³ was injected into well 91 in order to repressurize the reservoir and thus reduce the secondary gas cap and to gain more data by the water flood performance about the planned flood concept. Formaldehyde was injected together with the water as a tracer and as a biocide for the following polymer slug.

A xanthan polymer solution containing 800 - 1000 ppm of active xanthan was injected into wells 90 and 91 at a rate of 10 - 12 m³/d in each well. Polymer injection started in November 1985 and ended in May 1988. The injection well head pressure was 1.5 - 2.0 MPa in well 90 and 1.0 MPa in

well 91. No injectivity problems occurred. Details about polymer mixing, injection and quality control are described elsewhere [1,2,3]

The project data are summarised in Table 2.

XANTHAN PROPERTIES

The xanthan used for the project was produced in a 40 m³ fermentor on a pilot scale by Bayer. The 2 % broth from the fermentor was transported to the field and directly diluted in the injection water to the desired concentration.

The fermentation process for xanthan was developed in order to obtain a product for enhanced oil recovery. This led to a product with a lower viscosity yield than xanthans used in other applications but a much better injectability. This was mainly due to the lower pyruvate content. The pyruvate group at the end of one side chain of the molecule (see Fig. 3) is mainly, in a similar way as the acetate group, responsible for the anionic character of the makromolecule.

In Table 3 the properties of all batches injected during the project period are listed.

PRODUCTION PERFORMANCE

Production in well 96 was started in March 1985. After producing 1200 m³ (V_n) of gas the well could produce at a rate of 3 - 4 m³/d with a water cut of zero. As this production rate was too low (only 25 % of the injection rate) and a further acceleration was not possible, well 88 was also put into production in May 1986 and well 86 in March 1987.

In Fig. 4 - 6 the water cut developments of these three wells are shown together with the results of a numerical reservoir simulation.

The reservoir simulation was performed with a black oil simulator and for the polymer prediction a polymer option [4] was used.

Although well 96 is the most distant from the injectors, a clear response to the polymer flooding could be observed very early on. In the beginning the measured data matched very well with the data predicted for water flooding. A decrease in water cut to 30 - 40 % could be observed in 1987, when the water cut predicted for water flooding should have been around 90 %.

Similar behaviour could be observed for well 86. This well was recompleted into another production zone at the end of 1988.

The water cut development for well 88 is shown in Fig. 5. This well is only 60 m from the injection well 90 and therefore a response to polymer flooding. The oil bank appeared very early on. For this well the agreement between the prediction for the water cut development by numerical reservoir simulation and the values measured in the field has also been very good. This is evidence of the values used as input for the simulation for adsorption and dispersion being reliable.

The simulation further showed, that about 50 % of the injected polymer was lost into the aquifer and therefore only a slug of about 35 % of hydrocarbon filled pore volume was used in the project for displacing the oil. Hence the observed effect in incremental oil recovery is remarkable. Up to the end of 1991 10 850 m³ oil had already been produced, which is more than that what was predicted to be the ultimate recovery for water flooding. In Fig. 7 a graph is shown, where the oil cut for the total block is plotted versus cumulative oil production.

The field results are compared with the predictions for water and polymer flooding. The simulation runs were performed until 1996 using the actual production rates and for further predictions the last actual production rates in the field. As can be seen from Fig. 7 cumulative production in the polymer flood is already higher than what may be extrapolated for water flooding. The actual field performance of the polymer flood is also better than the polymer prediction by numerical reservoir simulation. The incremental production by polymer flooding as compared to water injection is between 1000 and 1500 m³, which is 5 - 7 % of the original oil in place.

PRODUCED POLYMERS AND TRACERS

The amount of polymer and tracers in the produced fluids can give useful information about adsorption and stability of the chemicals in the reservoir. Tracers were the formaldehyde, which was injected as a biocide together with the xanthan and the salinity of the produced reservoir brine.

Samples were taken every 2 weeks from all the production wells and analysed for formaldehyde, salinity and polymer concentration.

Laboratory experiments had shown, that formaldehyde and xanthan only dissolved in the water and not in the oil. Therefore only the produced reservoir brine was analysed. The produced reservoir brine was separated from the oil and afterwards the water was filtered in order to remove suspended solids.

The analysis for formaldehyde was done by polarography, and the xanthan concentration was determined after dialysis by the phenol - sulphuric acid method [5].

Comparison with Numerical Simulation

In addition to the black oil simulation described above a simulation was carried out using a model, which was also capable of calculating the flow of tracers (SCORPIO).

In Fig 8 the results of this simulation with respect to the salinity development in well 88 are shown. The salinity of the original reservoir brine was 120 g/l, whereas the salinity of the injection water was 50 g/l. Fig. 8 shows that the field data and the results of the simulation fit very well, with the exception of early 1987, where water was produced from the layer below due to a casing leak.

Fig. 9 shows the results of the same simulation run with respect to formaldehyde. A retention of 15 µg/g for the formaldehyde was used in the simulation model. The results show that such a value describes the loss of formaldehyde in the reservoir quite well.

Fig. 10 shows the results for 2 different runs for the xanthan production in well 88. A retention of 15 and 40 µg/g was used for xanthan in the model. The results of the run using a retention of 40 µg/g fit best with the data obtained in the field.

The simulation runs were performed in 1988 and afterwards we had no opportunity to use this model again, so that only simulated data until the middle of 1988 could be used.

Nevertheless these results show, that the adsorption of xanthan in the field is between 30 and 40 µg/g. It should be mentioned that the field conditions with respect to adsorption of xanthan are relatively harsh, because of the high clay content, the low temperature and the high salinity.

Viscosity of Produced Xanthan

In Fig. 11 a flow curve for a fresh xanthan solution is shown together with flow curves of a xanthan solution produced from well 88, after it had been approximately 3 years in the reservoir. The flow curve of the xanthan solution produced from well 88 was measured before and after filtration. The filtered solution has a slightly lower viscosity than the unfiltered. But both flow curves are very similar to that of a freshly made solution of the same concentration. The more pronounced Newtonian region in the flow curves of the produced solution shows, that predominantly higher molecular parts of the xanthan are retained in the reservoir.

The fact, that the produced xanthan had still the same viscosity yield as the injected xanthan was the first indication that adsorption and degradation of the xanthan were only slight.

Molecular Weight of Produced Xanthan

The molecular masses of the fresh and the produced xanthan was determined by size exclusion chromatography (SEC) and low angle laser light scattering (LALLS). The following results were obtained for the samples, where the above flow curves had been measured. The results of these measurements may differ from other published data. Nevertheless they may be used for means of comparison of both samples.

Fresh sample: $M_w = 9.5 \cdot 10^6$ g/mole PDI = 1.39

Produced sample: $M_w = 9.3 \cdot 10^6$ g/mole PDI = 1.22

These results also suggest, that the polymer was hardly degraded. The lower polydispersity index (PDI) of the produced sample means a sharper molecular mass distribution and confirms the results of the flow curves, showing a more distinct Newtonian flow regime.

Chemical Analysis of Produced Xanthan Samples

Nine samples of produced polymer solution from well 88 were chosen for further analyses of chemical composition and intrinsic viscosities. Electron microscopy photographs were taken of these samples.

Preparation of the Samples.

The samples contained significant amounts of insoluble material, which was removed by centrifugation (12000 RPM, GSA rotor, 25°C, 30 min). The pellet was discarded.

The centrifuged samples apparently contained oil droplets. 100 ml of sample was shaken with 10 ml of toluene. The lower aqueous phase was recovered, and the non-polar phase containing the oil was discarded. It is assumed that this procedure does not affect the properties of xanthan.

In order to remove excess salts, including multivalent cations which might be strongly bound to the xanthan, the samples were dialysed against distilled water containing 10 mM HCl (3x) and finally distilled water on its own. About 30 % of each sample was freeze dried.

The rest of the samples were converted to the sodium form by continued dialysis against 10 mM NaCl and then distilled water. The samples, containing insoluble material, was centrifuged (pellet discarded) and filtered (pore size 0.45 μ m).

Analysis of Dissolved Carbohydrate

The concentration of xanthan was determined by the phenol-sulfuric acid assay (Dubois et al., 1956) [5]. Results are given in Table 4. The most diluted samples were

concentrated with a Centriprep 10 concentrator (Amicon) and analysed again (Table 4.).

Analysis of Chemical Composition

Freeze-dried samples were methanolysed (1.0 M HCl in anhydrous methanol, 80°C, 24 h), which cleaves all glycosidic bonds, yielding methyl glycosides. These were silylated with Sylon HTP and the mixture was analysed by gas liquid chromatography. (For more details on the method see Christensen & Smidsroed (1991) [6]).

The results (Fig. 12, Table 5) show that the chemical composition (Man/Glc and GlcA/Glc-ratios) of the side chains did not change significantly during the flood.

The GC-method also gives information on the pyruvate content, since the pyruvate-mannose bond is stable during the methanolysis (Dudman and Lacey, 1986 [7]), and yields a separate peak in the chromatogram apart from unsubstituted mannose. Fig. 13. shows that the pyruvate substitution is constant in the interval analysed, which also confirms that the mannose/glucose ratio must be constant.

Intrinsic Viscosity

To the dialysed samples were added NaCl to a final concentration of 10 mM and NaN_3 to 1 mM. Intrinsic viscosities were measured at 22°C using a low shear cartesian diver viscometer.

The results (Table 4) are uncertain due to low concentrations, but indicate some degradation. A 50% reduction in $[\eta]$ suggests an average of only one break in the polymer.

Electron Microscopy

A typical electron micrograph in Fig. 14 shows the fresh xanthan and the xanthan as produced from well 88. The method for how these micrographs are taken is described in reference [8]. The results are in accordance with the $[\eta]$ -data, showing normal ordered xanthan, but also some aggregates.

Bacterial Activity

Although hardly any degradation of the xanthan was found the presence of bacteria that could degrade xanthan was also investigated.

A strictly anaerobic specifically xanthan degrading fermentative microorganism was isolated by enrichment cultures from bottom residues of the oil water separator in the oil field Eddesse - Nord.

The same bacterium variety was also isolated from a natural salt water location.

The xanthan degrading bacteria only grow on xanthan. They do not utilise the following substrates: glucose, mannose, glucuronic acid, fructose, galactose, ribose, xylose, cellubiose, maltose, sacharose, lactose, cellulose, starch, dextran and pyruvate. The fermentation products of the xanthan degrading bacteria are: acetate, lactate and hydrogen. The formation of these fermentation products in the cell resulted through so-called glycolysis, which are also represented in higher organisms.

The optimum growth rate was found to occur at a pH value of 7 at 30 °C. The growth rate was inhibited at higher temperatures and at a NaCl concentration of less than 20 and more than 60 g/l.

Despite this relatively hesitant growth rate on xanthan, no xanthan depolymerase could be detected. However, as such an enzyme is required for the breakdown of xanthan, it still remains unclear why it could not be detected.

After the growth on xanthan, there still remained an unused proportion (up to 45% of the total carbohydrates) which had the same composition as xanthan. More xanthan was broken down in mix-cultures with hydrogen-using bacteria. In a mix-culture with another fermenting isolate, that could use not xanthan but could use monomer and oligomer sugars, it was shown that even more bacteria in the form of food competitors could grow during the xanthan degradation.

CONCLUSIONS

1. Polymer injection into the reservoir could be maintained during the whole project without any difficulties. Production of a xanthan with the necessary polymer quality could be achieved easily.
2. The project can be regarded as technically successful in terms of polymer injectability and incremental oil production.
3. The material balance of injected and produced polymer, as determined by numerical reservoir simulation, lead to adsorption values of 30 - 40 $\mu\text{g/g}$, which is lower than expected according to literature and our own laboratory measurements.
4. Degradation of the polymer was only slight, according to viscosity yield, molecular mass and intrinsic viscosity measurements.
5. No change in chemical composition of the xanthan was observed for the three years of residence in the reservoir.
6. A xanthan degrading species of bacteria, well adapted to the conditions in the oil water separator in the field,

could be isolated. However it could not degrade the xanthan significantly during the project period in the reservoir. If this is due to the biocide used, the low pH-value or the higher salinity in the reservoir, it will be verified in further investigations.

ACKNOWLEDGEMENT

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Table 1: Reservoir Data

Formation:	Sandstone	
Area:	21 150	m ²
Depth:	300 - 350	m
Thickness:	5	m
Pore Volume:	27 500	m ³
OOIP:	21 200	std m ³
Permeability:	0.3 - 1.2	μm ²
Porosity:	26	%
Oil Viscosity:	7	mPas
Oil Density:	841	kg/m ³
Bo @ BPP:	1.05	
Temperature:	22	°C
Salinity of Reservoir Brine:	120	g/l
Salinity of Injection Water:	50	g/l

Table 2: Project Data

Start of Polymer Injection:	Nov. 1985	
End of Polymer Injection:	May 1988	
Injected Polymer:	537	m ³ broth
	9 450	kg
Injected Polymer Solution:	15 500	m ³
	0.7	PV
Viscosity of Polymer Solution:	-12	mPas
Injected Formaldehyde:	40 000	kg
Incremental Oil Production:	1000-1500	m ³
	5-7	% OOIP

Table 3: Properties of Xanthan Batches

Batch	Pyruvate mass %	Acetate mass %	Molecular Mass /10 ⁶	Active Content of Broth %
0	1.00	0.65	7.91	2.15
1	2.29	0.91	7.24	0.95
2	2.04	0.65	8.44	2.29
3	2.42	0.78	8.99	2.38
4	2.11	2.23	9.43	1.72
5	2.50	2.57	7.12	1.90
6	1.83	0.97	7.54	2.27
7	2.29	1.20	8.23	2.07
8	2.27	0.89	8.05	1.90
9	2.00	1.84	10.52	1.69
10	2.47	1.72	12.20	1.25
11	2.50	1.66	9.81	1.75
12	2.30	1.29	11.18	1.70
13	2.87	1.87	12.71	1.55
14	2.48	0.85	7.47	1.49
15	2.35	1.21	8.64	1.83
16	2.53	1.13	12.59	1.86
17	2.15	1.36	8.23	1.69
18	2.32	2.63	8.83	1.84
19	2.63	1.46	8.40	2.01
20	1.86	1.33	7.97	1.79
21	1.00	0.67	9.81	1.62
22	1.81	0.96	8.70	1.36
23	1.94	1.11	6.15	1.36
24	1.17	0.71	5.06	1.43
25	2.50	1.38	8.79	1.40
26	2.29	2.71	6.21	1.60
average	2.15	1.36	8.75	1.79

Table 4: Intrinsic Viscosity

Sample No.	Sample Date	Concentration ² (mg/ml)	Intrinsic Viscosity [η] ³ (ml/g)
1	broth	1.41	2400
2	89/07/17	0.038	3000
3	88/12/09	0.0032	
4	88/01/13	0.180	1200
6	89/08/31	0.0052	1200
6	89/08/31	0.0015	500 -1300 ⁴
7	89/01/05	0.0021	500 -1500 ³
8	88/04/12	0.149	3000
9	87/12/18	0.142	1000
10	88/03/08	0.159	1500

² calculated as Na-xanthan (pyruvate and acetate free)
³ relative uncertain: minimum 10 - 20 %
⁴ determination uncertain because of low polymer concentration

Sample	Man/Glc	GlcA/Glc	Pyruvate %
1a	1.15	0.58	25.2
1b	1.09	0.55	24.8
1c	1.10	0.59	27.1
9a	0.96	0.49	21.2
9b	0.90	0.49	21.8
9c	0.90	0.41	19.8
4a	0.93	0.47	20.4
4b	1.09	0.48	18.5
4c	0.94	0.51	21.2
10a	0.99	0.55	23.5
10b	0.98	0.54	22.6
8a	1.22	0.69	25.8
8b	1.13	0.63	22.9
8c	1.02	0.53	21.1

Man/Glc: Molar ratio mannose:glucose GlcA/Glc: Molar ratio glucuronic acid:glucose
 Pyruvate %: 100 % corresponds to fully xanthan (1 pyruvate per repeating unit) sample 1 is reference made of fresh xanthan broth

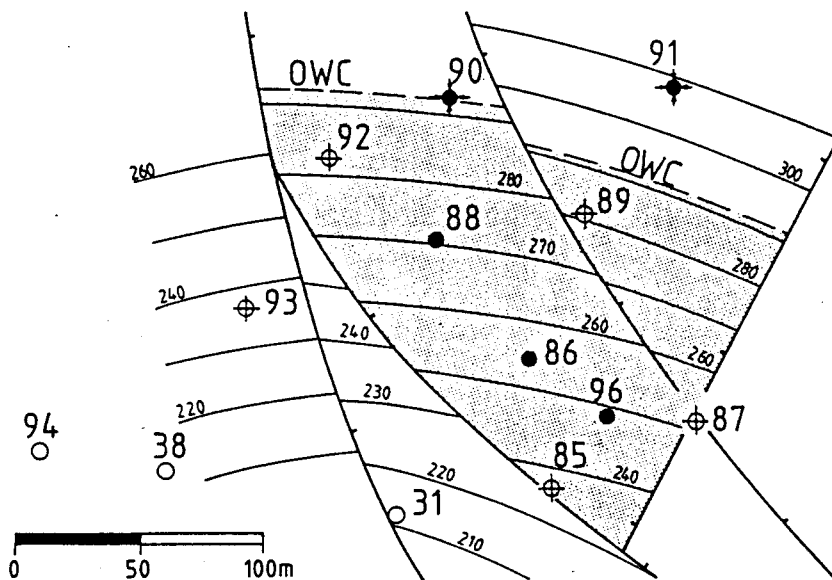


Fig. 1: Structure map of pilot area

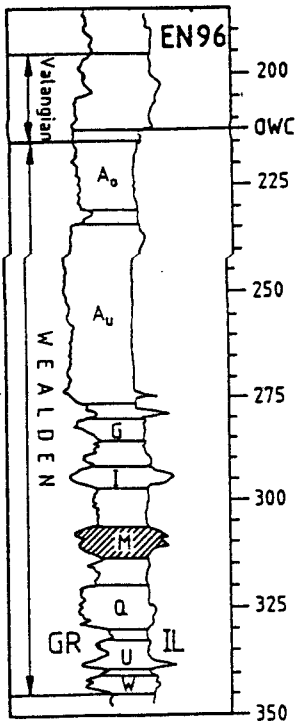


Fig. 2: Log of well 96

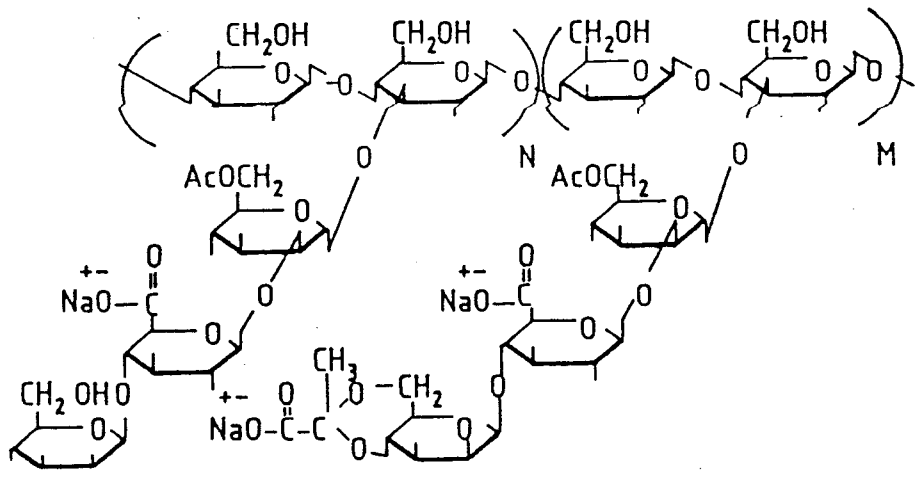


Fig. 3: Xanthan molecule

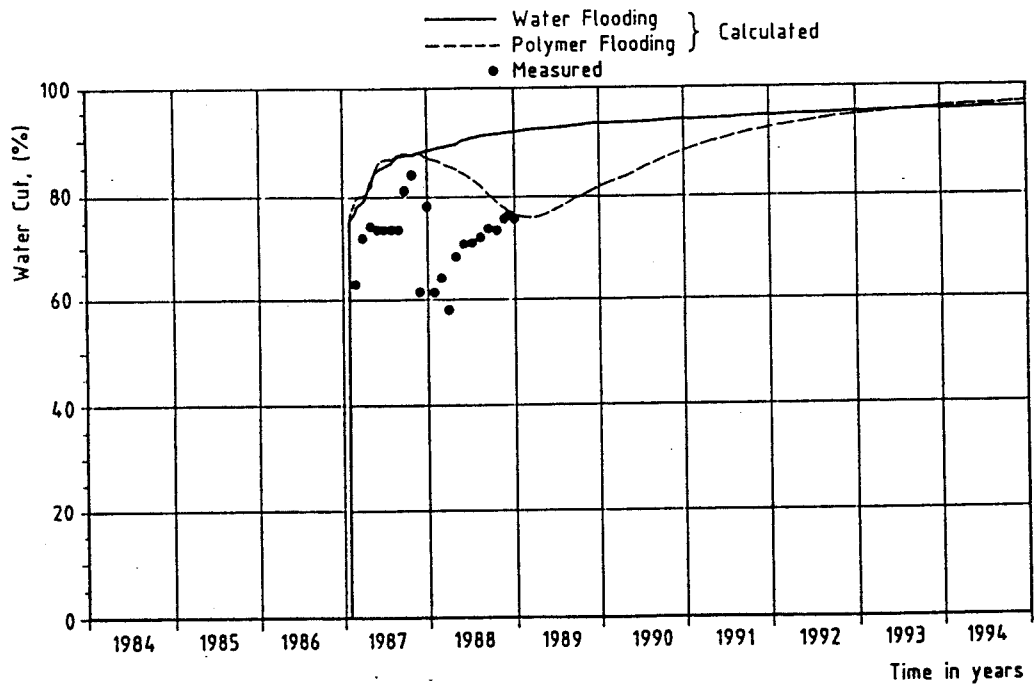


Fig. 4: Water cut development of well 86

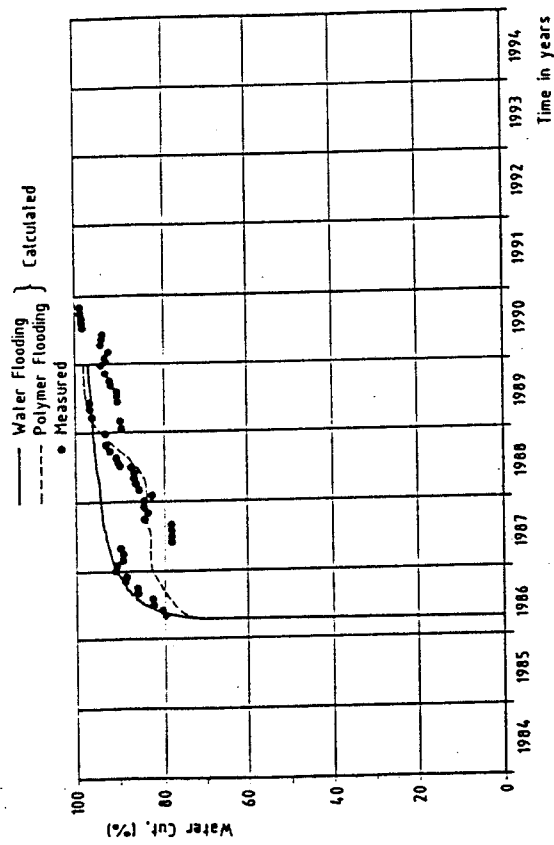


Fig. 5: Water cut development of well 88

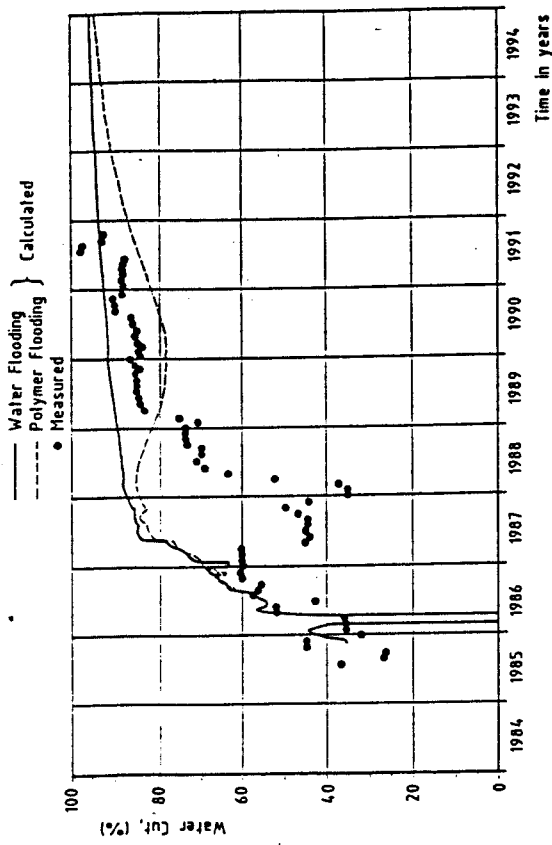


Fig. 6: Water cut development of well 96

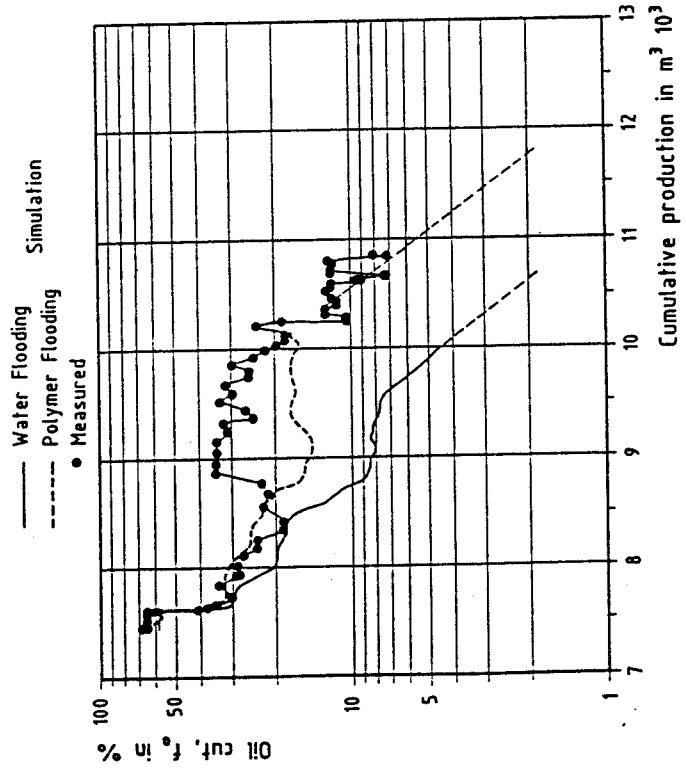


Fig. 7: Oil cut vs. cumulative oil production

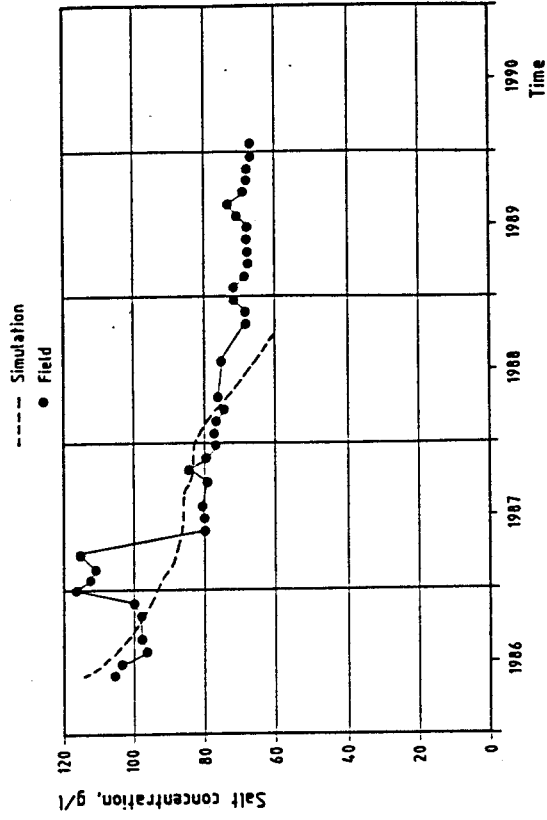


Fig. 8: Field results and simulation of salinity development in well 88

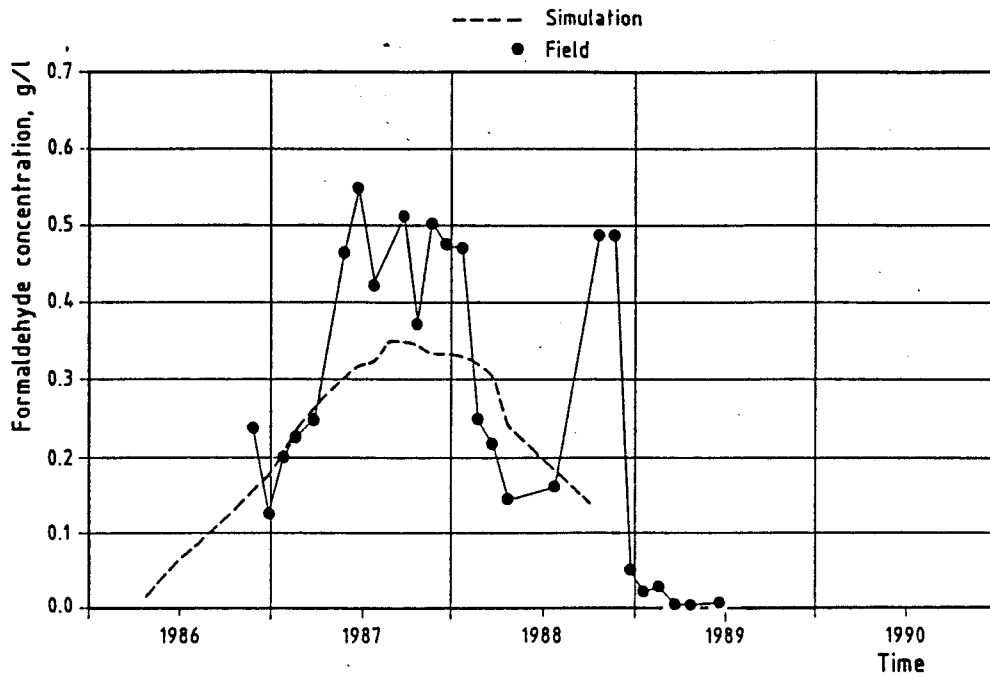


Fig. 9: Field results and simulation of formaldehyde production in well 88

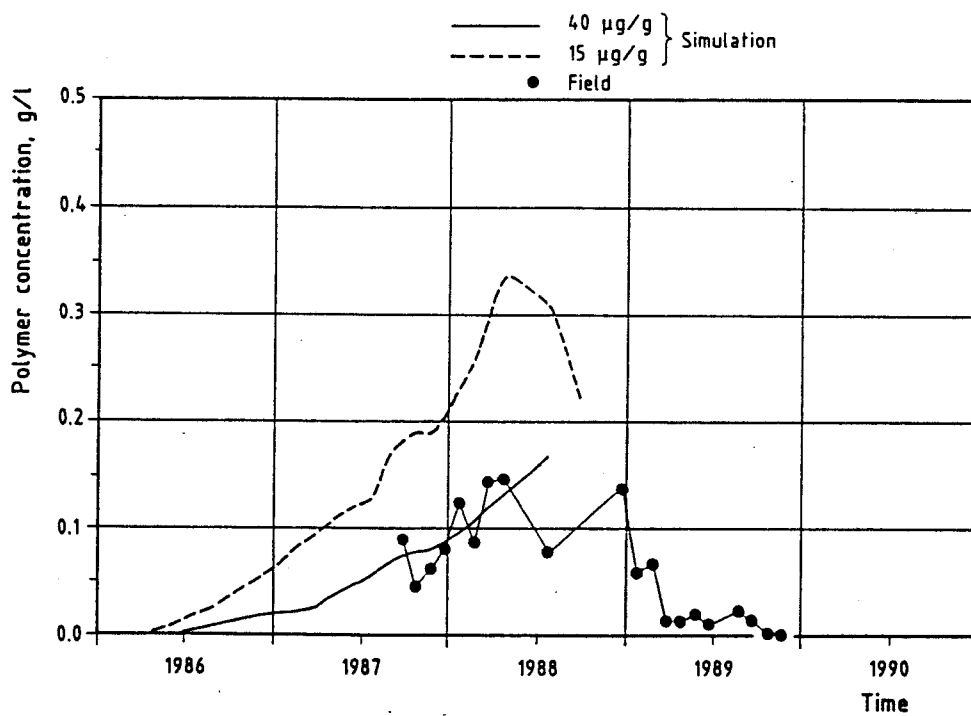


Fig.10: Field results and simulation results of xanthan production in well 88

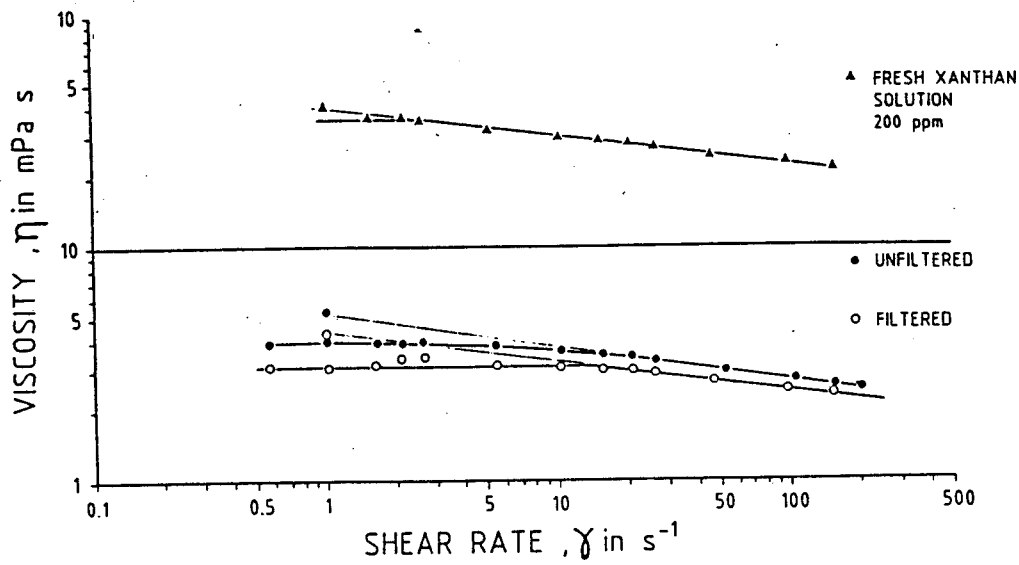


Fig.11: Flow curves of fresh and produced xanthan

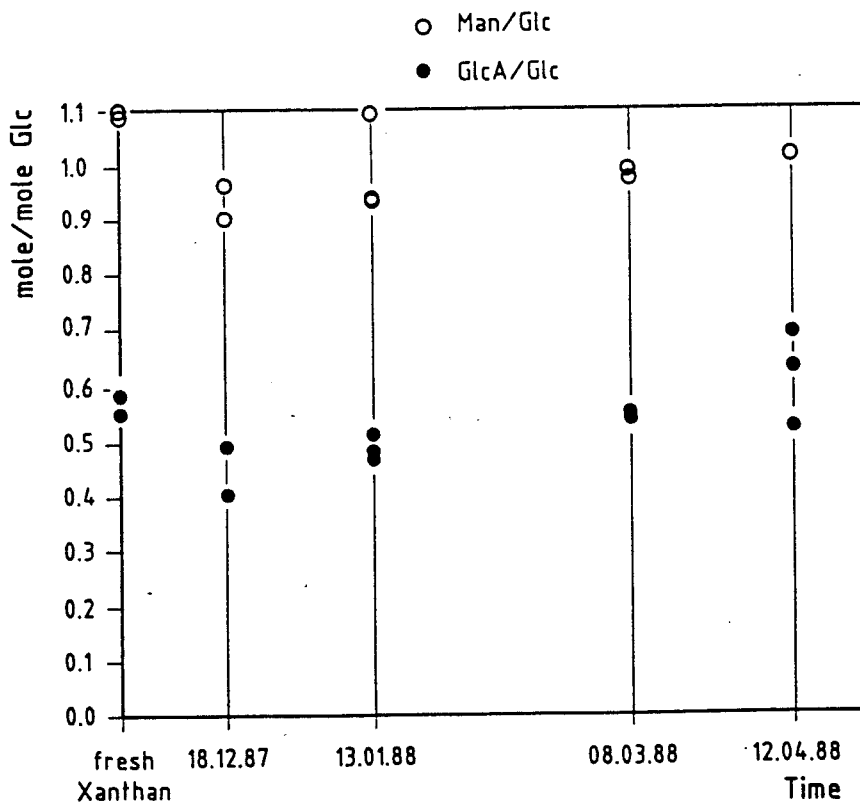


Fig.12: Relative sugar composition of xanthans produced from well 88

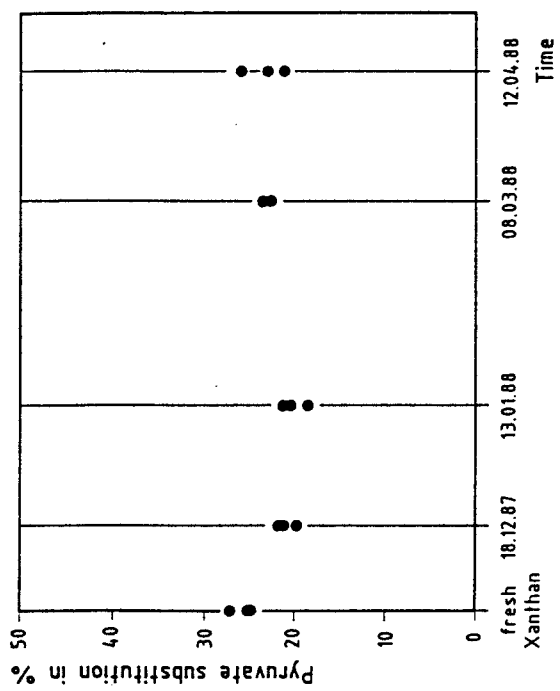


Fig.13: Pyruvate substitution

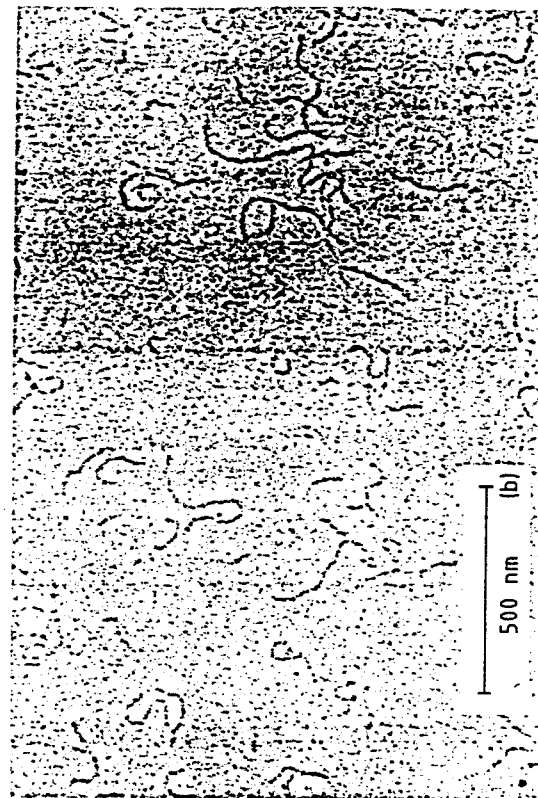
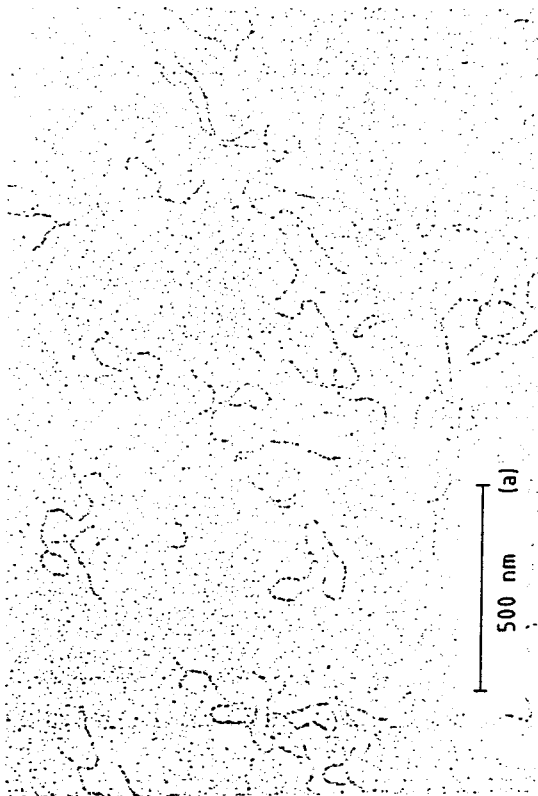


Fig.14: Electron microscopy photograph of fresh xanthan (a) and produced xanthan (b)