

Screening of Xanthan-Biopolymer for a High Salinity Oil Reservoir

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Abstract: For a North-German oil reservoir with a salinity of the reservoir brine of 220 g/l TDS a screening of different commercially available xanthans was carried out. While developing this screening procedure the experience gained in the xanthan pilot project Eddesse-Nord was considered. For the screening a mixing process to obtain a good injectable polymer solution was developed for the different products that is also applicable in the oil field. Other screening criteria were the viscosity yield, the injectability and the retention/adsorption. It was found that the xanthans tested behave very different with respect to viscosity yield and injectability. The molecular weights and molecular weights distributions were determined using SEC/LALLS. The solution properties were characterized by measuring intrinsic viscosities. The adsorption characteristics of the different xanthans on quartz-sand and reservoir-sand were compared by measuring heats of adsorption using a micro-flow-calorimeter.

1. Introduction

A polymer pilot flood project was planned for a North-German oil field with a high salinity reservoir brine. This brine was also to be used as mixing water for the polymer. As the viscosity of the oil is relatively low and the reservoir rather homogeneous, the recovery possible by water flooding is already 40 %. The reservoir data are given in Table 1.1.

A simulation study showed that an incremental oil recovery of 6 - 8 % of the original oil in place is possible by polymer flooding.

The screening of a suitable polymer for this project is subject of this paper. As fresh water was not available for flooding, and so flooding with polyacrylamides was not possible, different commercially available xanthans were tested. The objective was to find a xanthan with a good viscosity yield at acceptable price and costs for mixing and storage and with a good injectability and low adsorption.

Table 1.1: Reservoir data

Reservoir type:	Sandstone	
Depth:	1300	m
Temperature:	56	°C
Salinity of brine:	210	kg/m ³
Calcium:	5.1	kg/m ³
Oil viscosity u.r.c.:	3.5	mPa·s
Average permeability:	1	μm ²
Average porosity:	27	%

Table 1.2: Commercial polymer samples used for screening

Product	Type	c _s %	c _a %	M _w 10 ⁶ g/mole	c _{py} %
A1	Ferm.broth	2.78	2.12	8.54	2.76
A2	Conc.broth	9.76	9.02	8.97	2.76
B1	Conc.broth	9.62	7.38	9.85	1.77
B2	Conc.broth	12.53	10.83	11.47	2.89
C	Powder	96.38	95.65	10.58	3.74
D	Conc.broth	9.56	7.92	10.68	4.13
E1	Conc.broth	8.78	8.30	11.61	5.69
E2	Conc.broth	8.19	7.88	12.14	6.08

c_s is the total solid content, c_a is the content of active matter, c_{py} is the pyruvate content.

Samples of different commercial xanthan products were tested for their applicability in this project. The samples and their properties are listed in Table 1.2. The names of the suppliers are coded.

2. Screening Methods and Criteria

2.1 Mixing procedure

2.1.1 Xanthan broth

Xanthan broths were received in different concentrations. It was found that mixing of unconcentrated fermentation broths with a content of active matter of 1.5 - 2 % was easier than mixing concentrated broths with an active material of 8 - 10 %. It was necessary to dilute the concentrated broths first in fresh water before diluting to the final concentration with brine. So all broth-samples were first diluted with fresh water to a concentration of 5000 ppm. These stock solutions were sheared through shear plates and then mixed with the brine. The polymer solutions were then stirred in a beaker and afterwards sheared again. These solution were degassed by applying vacuum. The solutions could then be used for injectability testing and for measuring flow curves. The mixing procedure is schematically shown in Fig. 2.1.

2.1.2 Xanthan powder

Powder mixing was done similarly to the mixing of the broths. A concentrated solution was made in fresh water and then the same steps as in mixing broths were performed as shown in Fig. 2.1.

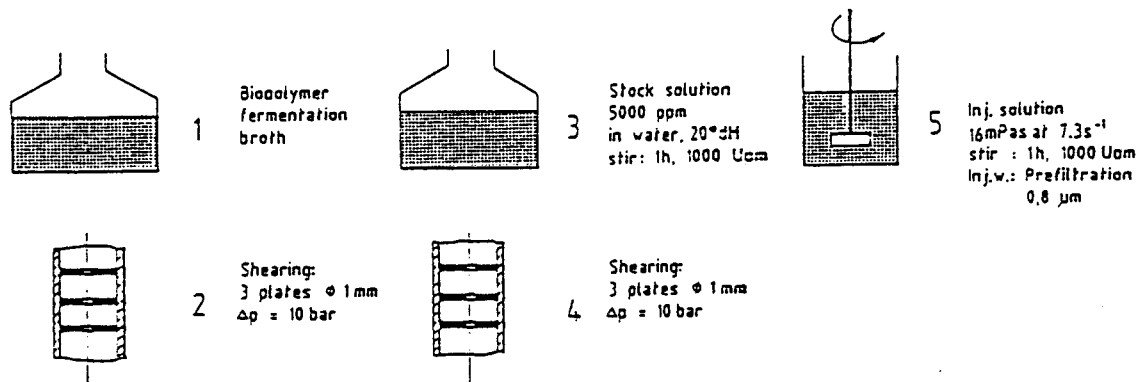


Fig. 2.1: Diluting and mixing procedure for xanthan broths

2.2 Injectability

A solution of the polymer in the mixing water should fulfil the following requirements of an injectivity test: The polymer solution is injected into a sand pack, the pressure drop across the sand pack is recorded during the injectivity test which lasts about 18 h, the ideal case is that the pressure drop remains constant during the whole test. The maximum increase of the pressure drop measured 1h after the start of the polymer flood should not exceed 30 % during the next 15 h. Higher values were not tolerated. The tests were performed at room temperature. The data of the sand pack are listed in Table 2.1.

Table 2.1: Data of the sand pack

Sand:	broken quartz sand
Grain size:	63 - 90 μm
Length:	4 cm
Diameter:	1.9 cm
Porosity:	50 - 55 %
Permeability:	2 - 3 μm^2

After the injectivity test the residual resistance factor R_{ff} was measured by flooding with the mixing water. The pressure drop expected theoretically was calculated using the relation suggested by LITTMANN (1988). The residual resistance factor should be 1 - 3.

2.3 Viscosity Yield

Flow curves were measured in a Haake rotational viscometer using a double cylinder system. The solutions were made up in a way that they all had a viscosity of 16 mPa·s at a shear rate of 7.3 s^{-1} . This was done to make all polymer products comparable, especially, for the injectivity test. The concentration needed for this viscosity was used to compare the viscosity yield of the different products.

To characterize the different xanthans, molecular weight was measured by Size Exclusion Chromatography (SEC) and Low Angle Laser Light Scattering (LALLS). Polydispersity was used as a measure for the molecular weight distribution (HERBST 1988).

Intrinsic viscosity was measured to characterize the solution properties.

The pyruvate content was measured using the enzymatic test procedure as described by SANDFORD et al (1977).

A high-pyruvate, high-molecular weight xanthan was treated by ultra sonication to reduce the molecular weight. So it was possible to examine the dependence of the properties of one product on molecular weight at a constant pyruvate content.

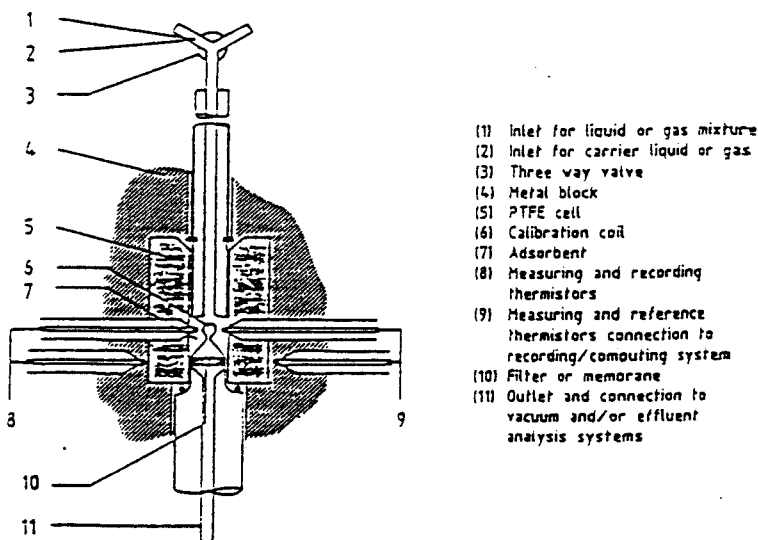


Fig. 2.3: Micro-flow-calorimeter

2.4 Adsorption

Adsorption of the different xanthans was characterized by measuring the heat of adsorption in a micro-flow-calorimeter. The xanthan solution was flooded through a pack of the prepared rock sample in the calorimeter. The setup of the apparatus is shown in Fig. 2.3. The mass of the samples was appr. 230 mg, the resolution of the calorimeter was 0.1 mJ, so that the small heats of adsorption of xanthan on the rock surface could be measured.

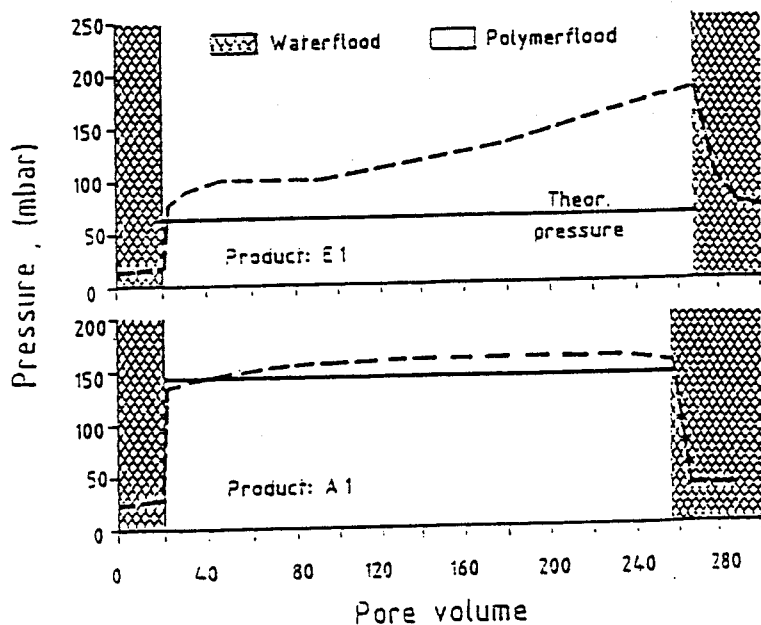


Fig. 3.1: Typical results of an injectability test for well and poorly injectable polymer solution

Table 3.1: Results of injectivity testing

Product	c_p kg/m ³	p %	R_{ff} -	n -	H mPa·s ⁿ	M_w 10 ⁶ g/mole	c_{py} %
A1	0.780	14	1.4	0.685	32.5	8.5	2.7
A2	0.645	3	1.6	0.684	31.0	8.9	2.76
B1	0.600	458	1.9	0.685	33.5	9.8	1.77
B2	0.535	670	25.5	0.659	32.1	11.4	2.89
C	0.435	13	2.1	0.602	38.5	10.5	3.74
D	0.300	14	1.6	0.528	49.0	10.6	4.13
E1	0.370	83	4.2	0.607	35.0	11.6	5.69
E2	0.370	626	30.0	0.655	27.0	12.1	6.08
E1a	0.620	485	13.5	0.656	33.7	10.0	5.69
E1b	0.895	2143	52.1	0.677	35.3	8.5	5.69
E1c	1.365	2237	88.0	0.720	31.2	7.0	5.69

3. Results

3.1 Injectability

The injectability of different polymer solutions was tested as described above. Typical results are shown in Fig.3.1 for a well (A1) and a poorly (E1) injectable polymer solution. The pressure drop for the well injectable polymer solution was 150 mbar, the pressure drop remained nearly constant during the whole experiment and the pressure drop measured was the same as calculated and the residual resistance factor was 1.4. For the poorly injectable solution the pressure drop was lower due to the different flow curve, but it was also higher than calculated and it was steadily increasing, the increase in pressure drop was 83 % and the residual resistance factor was 4.2. This means that this polymer solution did not satisfy the criteria described above. The results of all injectivity tests are listed in table 3.1 together with the data of the flow curves, molecular weights and pyruvate contents.

3.2 Polymer Properties

Solutions of different xanthans were tested as described above. The results are summarized in Table 3.2.

The polydispersity index P_{DI} is defined as the ratio of M_w/M_n . The specific viscosity is $\mu_{sp} = (\mu - \mu_0)/\mu_0$ where μ_0 is the viscosity of the solvent, which is 1.16 mPa·s for the brine at 20 °C and 1 mPa·s for the potassium-phosphate solution. k_2 is the second coefficient in the virial equation for the specific viscosity $\mu_{sp} = k_0 + k_1 c + k_2 c^2 + \dots$; this means k_2 is the slope of the straight portion in the plot of the reduced viscosity $\mu_{red} = \mu_{sp}/c$ versus the polymer concentration c , whereas the intrinsic viscosity is $[\mu] = k_0/c + k_1$. The slope k_2 is often expressed according to the Huggins formula as $k_2 = k'[\mu]^2$. k_2 is a measure for the quality of the solvent. An ideal solution in which the molecules of the polymer do not interact has a k_2 of zero, a k_2 of infinity

Table 3.2: Molecular weights and solution properties of different xanthans

Product	Mw* 10 ⁶ g/mole	P _{DI}	μ_{sp} * kg/m ³	c ₁₆ kg/m ³	$[\mu]$ m ³ /kg (m ³ /kg) ²	k ₂	c _{py} %	k'
A1	8.5	1.74	13.6	0.780	4.0	15	2.76	0.94
A2	8.9	1.52	17.8	0.645	5.7	14	2.76	0.43
B1	9.8	1.39	0.600	0.600	3.7	6	1.77	0.44
B2	11.4	1.22	26.0	0.535			2.89	
C	10.5	1.25	37.6	0.435	7.4	24	3.74	0.44
D	10.6	1.35	31.3	0.300	9.8	18	4.13	0.19
E1	11.6	1.16	41.8	0.370	8.2	23	5.69	0.32
E2	12.1	1.14	45.3	0.370			6.08	
E1a	10.0		21.5	0.620	5.3	7.3	5.69	0.28
E1b	8.5		10.0	0.895	3.3	7.2	5.69	0.66
E1c	7.0		5.9	1.365	1.9	13	5.69	3.60

*) measured in a 0.1 m potassium-phosphate solution at a concentration of 1 kg/m³

means that the product is not soluble. c₁₆ is the concentration needed to obtain a viscosity in the brine of approximately 16 mPa·s at a shear rate of 7.3 s⁻¹; c_{py} is the pyruvate content.

Specific viscosity correlates very well for all products according to the equation $\mu_{sp} = kM_w^\alpha$ with the constants $k = 7.44 \cdot 10^{-21}$ and $\alpha = 3.073$. Intrinsic viscosities were measured in a Zimm-Crothers viscometer.

It is obvious that the high molecular weights correspond with high pyruvate contents as shown in Fig. 3.2, which is the reason that usually high pyruvate xanthans show a good viscosity yield.

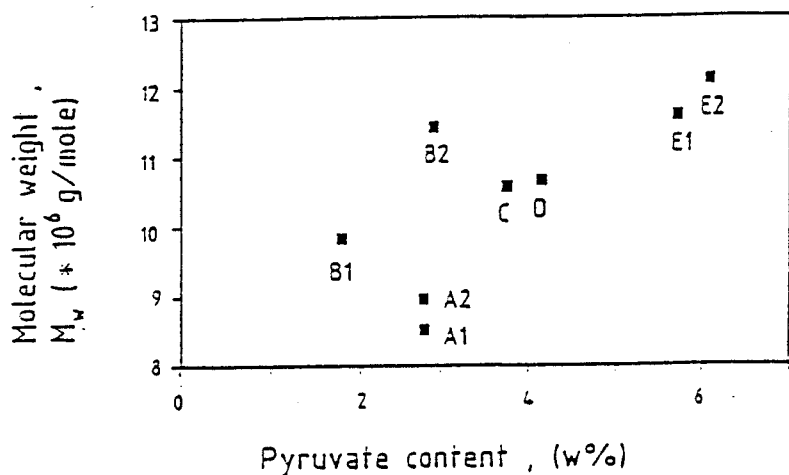


Fig. 3.2: Correlation between molecular weight and pyruvate content of different xanthans

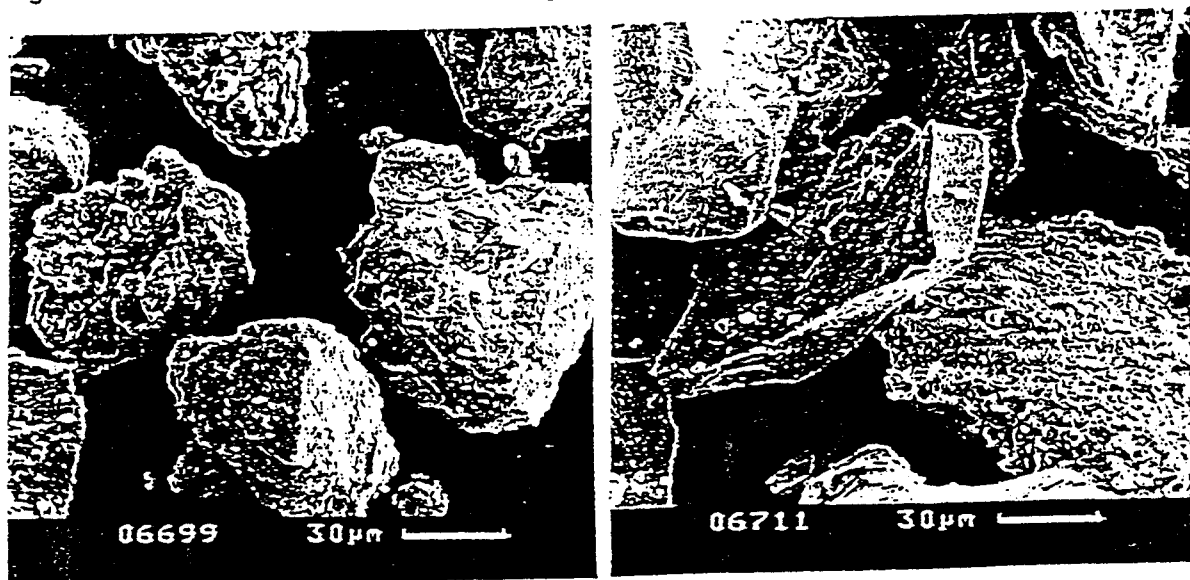


Fig. 3.3: SEM-micrographs of reservoir rock and clean quartz sand

3.3 Adsorption

Adsorption of the products A1, E1 and C was measured as described above in a micro-flow-calorimeter. As adsorbents two types of rock were used: a cleaned oil saturated reservoir rock and a pure quartz sand. For the measurements the same grain size distribution of the sands were used

as in the injectivity tests. SEM-micrographs are shown in Fig.3.3. The adsorption tests were performed in a 50 g/l TDS reservoir brine.

Table 3.3: Results of adsorption measurements. Heats of adsorption measured in a micro-flow-calorimeter

Adsorbent	Spec. Surf. S_o m^2/g	Adsorptive	Heat of Ads. H_{ads} mJ/g
<u>Res. Sand</u> 63-90 μm	2.620	Xanth. A1	16
		Xanth. C	31
		Xanth. E1	-
		Glucose	< 1
		Na-pyruvate	5
<u>Quartz</u> 63-90 μm	0.195	Xanth. A1	150
		Glucose	< 1
		Na-pyruvate	< 1

This brine was chosen to make the results comparable to other adsorption measurements from flood tests in this water; in addition to the polymers also the adsorption of the monomers glucose and pyruvate was measured. The data and the results are listed in Table 3.3.

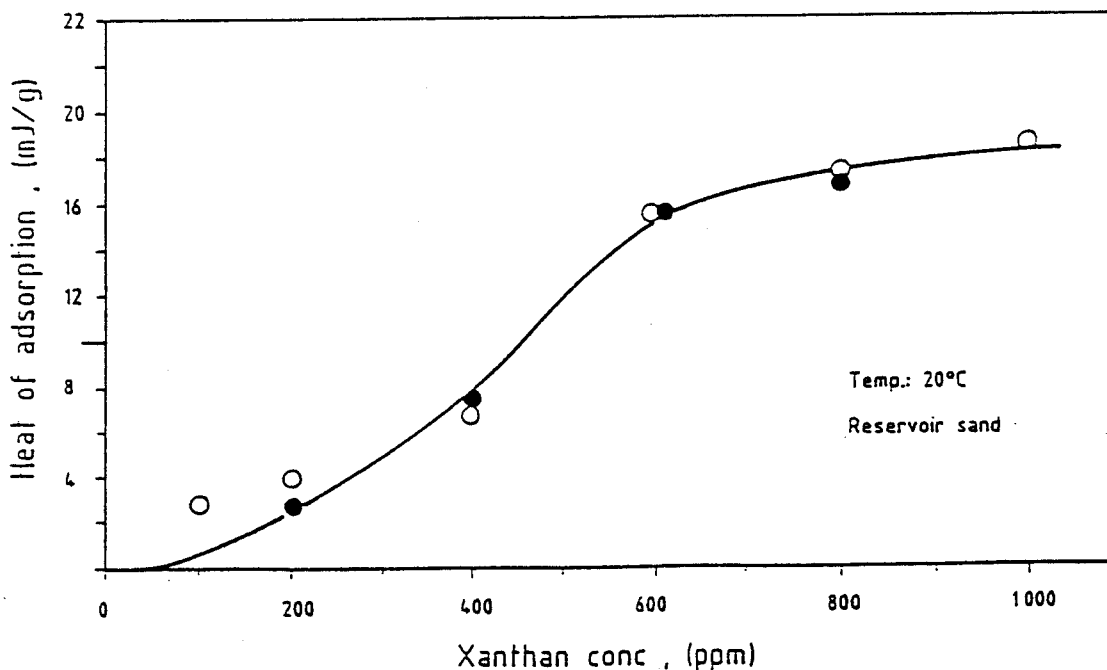


Fig 3.3: Adsorption isotherm measured at reservoir rock for xanthan A1

The adsorptives were dissolved in the reservoir brine at the concentration of 1000 ppm. The calibration of the heats of adsorption to an absolute amount of adsorbed material was done using the results of a flood experiment with the same material. An adsorption of 32 $\mu g/g$ was found on clean quartz sand. In Fig. 3.3 an adsorption isotherm for the heats of adsorption is shown. The specific surfaces were measured in the micro-flow calorimeter using n-Butanol in n-Heptan (TEMLER).

4. Discussion

Eight commercially available xanthans from five different producers were tested for their applicability for polymer flooding under the above described reservoir conditions. The products had molecular weights between $8 \cdot 10^6$ and $11 \cdot 10^6$ g/mole and showed therefore different viscosity yields. A clear correlation between molecular weight and viscosity yield was found.

Only four products from three different producers satisfied the injectability test at the above described conditions. It should be mentioned that some of the products that failed in the tests herein showed a better injectability in fresh and distilled water.

A correlation was found between pyruvate content and molecular weight. Higher molecular weights were found at higher pyruvate contents. The reason for this may be that at higher pyruvate contents higher intermolecular forces lead to an increased aggregation, especially in high salinity brines.

So the main reasons for a poor injectability were found in a high molecular weight, which usually corresponds with high pyruvate contents and thus the tendency to form aggregates. One sample with a low pyruvate content and an medium molecular weight (B1) also showed bad injectivities, but the reason here is that the sample was spoiled with solid particles.

The measurements of the intrinsic viscosities cannot easily be interpreted. The problems in measuring intrinsic viscosities of xanthan solutions will be discussed elsewhere (KULICKE 1989)

It was found that adsorption of xanthan is not automatically high on surfaces with higher area. Here it is important that the adsorption sites are accessible to the macromolecule, which is obviously not the case for all sites of the reservoir rock (see Fig.3.3). The reservoir rock has a specific surface of $2.6 \text{ m}^2/\text{g}$, but only a small part of this surface seems to be accessible to the big polymer molecules. The major part of the specific surface measured with the very much smaller n-Heptane-molecules is contributed by a fine structure on the grain surfaces. Furthermore the adsorption sites of the reservoir rock, that was originally oil saturated and then cleaned with solvents, seem to be less active than the adsorption sites on the clean quartz sand. Adsorption of xanthan was even higher on the quartz sand than on the reservoir rock sample.

The results from experiments performed with glucose and pyruvate clearly show that adsorption is influenced by the pyruvate content of the molecule, which means that higher pyruvate xanthans have higher adsorption, which in turn may also be an additional reason for the poor inject-ability that was found with these products. Unfortunately these products could not be tested in the micro-flow-calorimeter, as this requires a good injectability to avoid heat effects due to uncontrolled pressure increases.

Acknowledgement

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