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Research On The Polymer Concentration In The Gel Produced Liquid Detected By Fixed Nitrogen Method

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Abstract: In order to accurately determine the polymer concentration in the produced liquid of gel profile control and flooding well, the standard curves of polymer solution and polymer gel are drawn by using the method of fixed nitrogen. The standard curve is optimized by the physical simulation results of the polymer concentration in the produced liquid. The sixteen production wells in the gel test area of Daqing Oilfield are extracted randomly, and the fixed nitrogen and starch cadmium iodide method are used to detect the polymer concentration in the produced liquid. The error of test results is analyzed and the corresponding empirical formula is fitted. The research results provide an accurate and effective method for the detection of polymer concentration in the gel produced liquid.

Keyword: polymer concentration**;** polymer gel; fixed nitrogen method; error analysis; empirical formula

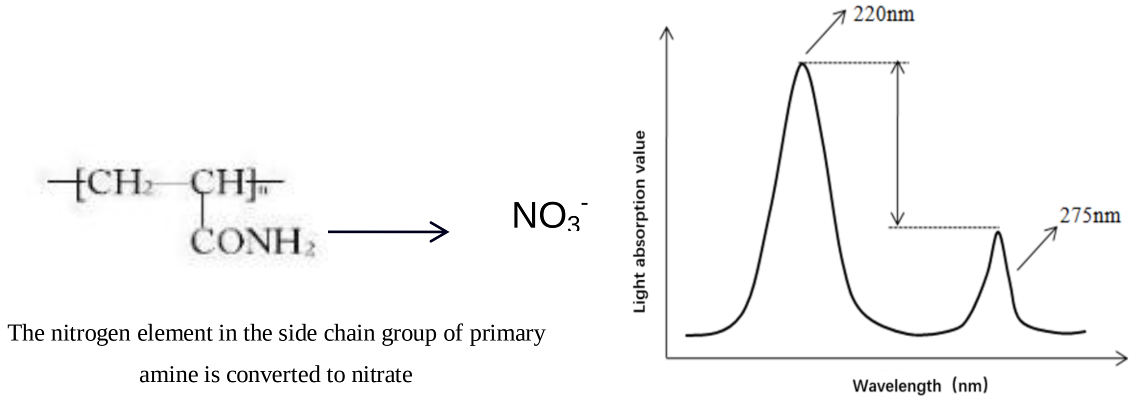
The detection of polymer concentration in the produced liquid plays an important role in dynamically monitoring the production process and evaluating the gel flooding effect. It is also one of the targets for controlling the discharge of sewage in the gel test area [1,2]. However, in the process of detection, the concentration of polymer obtained by using different standard curves of the same sample (polymer solution and polymer gel) was significantly different. At the same time, starch cadmium iodide method is commonly used to detect polymer concentration in oil field, but the dilution ratio of this method is too high, the operation process is relatively complex, and it is easy to introduce human error in measurement, resulting in relatively large relative error (about 20%) [3-5]. Compared with the starch cadmium iodide method, the detection error of nitrogen determination method is smaller (less than 5%), which has the characteristics of strong timeliness and accurate method. The non-volatile harmful drugs are used, but special instruments are needed in the operation process, the equipment is expensive and the cost is high [6].

In view of the above problems, the standard curve of polymer solution and polymer gel was plotted respectively by using nitrogen fixing method, and the standard curve was selected according to the physical simulation test results of polymer concentration test of produced liquid. 16 oil wells in gel test area of an oil production plant in Daqing oilfield were randomly selected, and the polymer concentration of produced liquid was detected by nitrogen fixing method and starch iodine cadmium method respectively. The error analysis and fitting empirical formula of the test results were carried out. The research results can provide reference for the analysis of the variation rule of the concentration of the produced liquid and the application of gel flooding technology, which is of great theoretical significance and application value.

I. EXPERIMENTAL PART

1.1 Experimental principle

The experimental principle of nitrogen determination method is to use potassium persulfate to oxidize ammonia nitrogen, nitrite nitrogen and most organic nitrogen compounds in water samples to nitrate (see Fig. 1 - (a)). Based on Lambert Beer law, the content of amide group on polyacrylamide in the produced solution can be identified and determined according to the unique and fixed absorption spectrum curve, so as to obtain the polymer concentration in the solution. Because the nitrate ion has the maximum absorption at 220nm, but the dissolved organic matter also has absorption here, which interferes with the determination; the nitrate ion has no absorption at 275nm, but only the dissolved organic matter has absorption, so the absorbance determination at 275nm is used to correct the nitrate nitrogen value [7,8]. The total nitrogen is $A = A_{220} - 2A_{275}$, The relationship between absorption value and wavelength is shown in the fig 1-（b）.The detection instruments include WTW 6100 VIS spectrophotometer, cr3200 digestion instrument, 10 mg / L ~ 150 mg / L total nitrogen measuring tube (14763) and its accompanying drugs N-1K、N-2Kand N-3K from Spectroquant company.



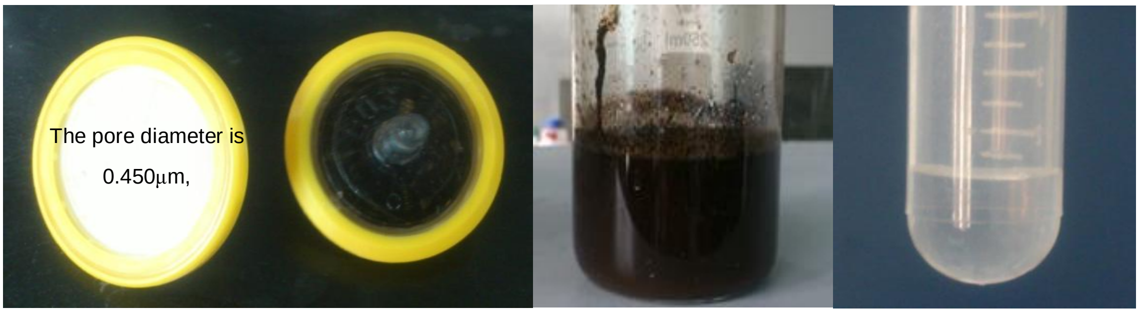
（a）Basic principles （b）Relationship between absorbance and wavelength

Fig. 1 Schematic diagram of experimental principle of nitrogen determination method

1.2 Operation steps

（1）Experimental method of polymer concentration in produced liquid microfiltration membrane filtration

The quantitative produced liquid is absorbed with a syringe, and the microfiltration membrane pinhead filter is inserted. Filtration is realized by manually pushing the syringe to remove suspended matter, oil and other impurities and eliminate error interference factors. Comparison of microfiltration membrane and water sample before and after filtration is shown in Fig. 2.



（a）Comparison of microfiltration membrane before and after filtration （b）Comparison of water samples before and after filtration

Fig. 2 Microfiltration membrane filtration

(2）Experimental method of injection fluid

①The spectrophotometer is zeroed by using the standard tube of total nitrogen.

Insert the total nitrogen standard tube, press ZERO BLANK and take it out after zeroing; insert the COD measuring tube and take it out after the COD tube number and range are displayed in the window, press ZERO BLANK, and insert the total nitrogen standard tube and take it out after zeroing.

②Determination of total nitrogen in polymer

Measure 1ml of the prepared solution in an empty tube, add 9ml of secondary water; add 1 spoonful of N-1K, 6 drops of N-2K, shake well; put it in a digester, digest at 120 ℃ for 1 hour; after digestion, take it out and let it stand and cool to room temperature; after shaking well, measure 1ml of digested sample, add 1ml of N-3K into the total nitrogen measuring tube, tighten the tube cover, shake well, and measure after 10min. The polymer concentration is calculated as follows [9]:

$$C_p \times \frac{(1-A)\times 14}{94A+(1-A)\times 71} = N \times S \tag{1}$$

Where, C_p is the concentration of polymer, mg / L; A is the molar hydrolysis degree of polymer,%; N is the total nitrogen value, mg / L; S is the dilution multiple.

1.3 Experimental materials

（1）Medicine and water

The polymer is partially hydrolyzed polyacrylamide dry powder (HPAM) produced by Daqing Refining and chemical company, with relative molecular weight of 1200 × 10^4 and solid content of 90%; the crosslinking agent and stabilizer are provided by Daqing Oilfield, with organic chromium as crosslinking agent andCr^{3+}content of 1.52%.

The experimental water is the sewage injected into Daqing Oilfield, and the water quality analysis is shown in Table 1.

Table 1 Water quality analysis

Ionic composition	Cation			Anion				Salinity
	Ca^{2+}	Mg^{2+}	K^{+}+Na^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	
sewage	44.37	14.95	1648.34	0.00	2349.27	1289.14	11.82	5357.89

（2）Core

The core is quartz sand epoxy resin cemented artificial core, the geometric size is: height × width × length = 4.5cm × 4.5cm × 30cm, the core gas permeability is about 600×10^{-3}μm^2.

1.4 Instrument and equipment

The experimental equipment mainly includes advection pump, pressure sensor, core holder, hand pump and intermediate container (Fig. 3). Except for horizontal flow pump and hand pump, other parts are placed in 60 ℃ incubator.

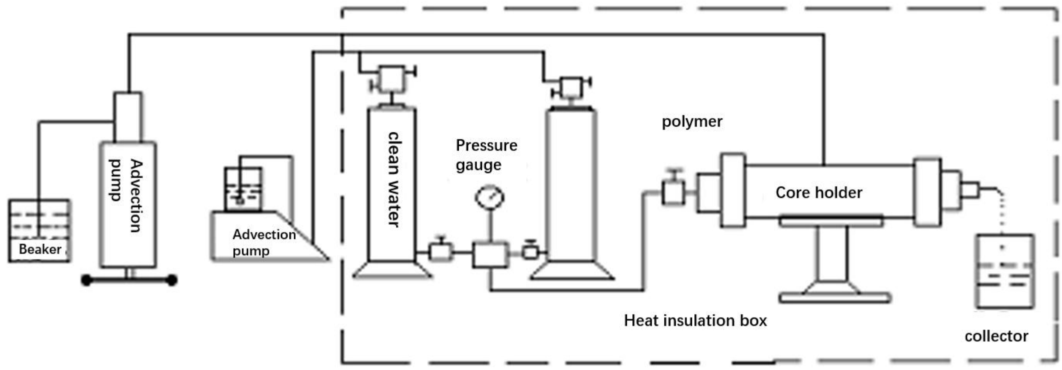


Fig. 3 Schematic diagram of equipment and process

Experimental steps:

① The core is evacuated and saturated to inject sewage;

② Inject 1.25pv chemical flooding agent and collect produced fluid;

③ Inject 0.25pv of follow-up water and collect produced liquid;

The injection rate in the above experimental process was 0.3ml /min.Before the experiment, the polymer solution was pre-shears to make its viscosity retention of 60%.

1.5 Conceptual design

Scheme 1: (draw standard curve) the polymer solution and polymer gel prepared from Daqing oilfield injected into sewage are diluted to a series of concentration standard solutions. The total nitrogen value is measured by nitrogen determination method. The standard curve of polymer solution and polymer gel is drawn by taking the solution concentration as abscissa and total nitrogen value as the ordinate, 800mg/L.

Scheme 2-1: the core is fully saturated with water, and then 1.25PV polymer solution (C_P = 800mg / L) is injected into the core, followed by water flooding until the pressure is stable.

Scheme 2-2: core saturation formation water, then injecting 1.25PV polymer gel (C_p=800mg/L) into core, followed by water drive to stable pressure.

Precautions: ① the total slug size of "chemical flooding + subsequent water flooding" is 1.5PV; ② the volume of each produced liquid sample is about 15ml from the beginning of chemical flooding.

II. RESULT ANALYSIS

2.1 Standard curve drawing

In program 1, the total nitrogen value of a series of polymer solutions and polymer gels was determined by the nitrogen determination method. The standard curves of polymer solution and polymer gel were plotted respectively, as shown in Fig. 4.

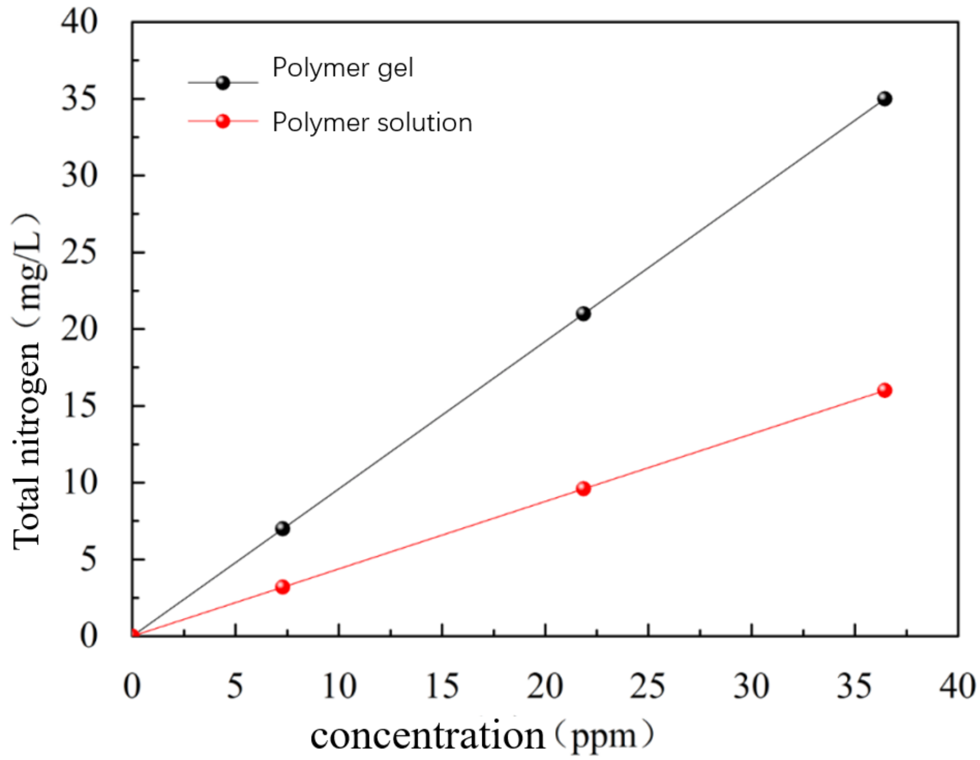


Fig. 4 Relationship between total nitrogen content and polymer concentration

It can be seen from Fig. 4 that under the same polymer concentration, the absorbance value of polymer solution and polymer gel is different, and the difference increases with the polymer concentration increasing. This is due to the role of Cr^{3+} in the polymer gel system as the carboxylic group of polyacrylamide molecules: the carboxyl groups in the polyacrylamide are ionized into carboxylic acids and hydrogen ions, and Cr^{3+} becomes polycyclic hydroxyl bridging ions through hydrolysis polymerization, and polyacrylamide forms and reacts with the polynuclear hydroxyl bridging ion to form polymer gel through carboxylic acid [10,11]. It can be seen that the crosslinking agent or stabilizer existed in the polymer gel reaction increased the total nitrogen value. At the same time, during the process of nitrogen determination, it was found that the solution in the test tube thickened and the bubbles increased after the gel solution was added to the reagent. From the principle of determining the polymer concentration by the nitrogen determination method, the gel solution contains some antioxidant components, which affects the detection value of total nitrogen.

2.2 Experimental study on polymer concentration detection of produced liquid

In "scheme 2-1" and "scheme 2-2", the concentration of polymer in produced liquid is detected by nitrogen determination method, and the detection results are shown in Table 2.

Table 2 Detection results of polymer concentration

Parameter / Scheme No	PV number	Sampling（mL）	light absorption value	Polymer concentration（mg/L）	
				Standard curve of polymer solution	Standard curve of polymer gel
Option2-1 (polymer solution)	0.3	0.3	0.331	86.09	—
	0.6	0.2	0.449	176.93	—
	0.9	0.1	0.299	234.59	—
	1.2	0.1	0.479	375.42	—
	1.5	0.1	0.380	298.31	—
Option2-2 (polymer gel)	0.3	0.3	0.291	76.06	36.43
	0.6	0.2	0.372	145.62	69.74
	0.9	0.1	0.277	217.23	104.04
	1.2	0.1	0.423	331.87	158.94
	1.5	0.1	0.352	276.25	132.30

As can be seen from table 2, the concentration of polymer obtained from the different standard curves (polymer solution and polymer gel) of the liquid samples in the "scheme 2-2" is quite different. When the standard curve of polymer solution is used for calibration, the polymer concentration is close to the test result of "scheme 2-1". Compared with "scheme 2-1" and "scheme 2-2", only the type of oil displacement agent is different, the former is polymer solution, the latter is polymer gel (mainly polymer, crosslinking agent and stabilizer concentration is low). When the oil displacement agent moves in the core pore, the polymer, crosslinking agent and stabilizer will be retained in the core pore, but because the polymer concentration is much higher than that of crosslinking agent and stabilizer, and the crosslinking agent and stabilizer are low molecular materials, the inaccessible pore volume is small, and the retention loss is large [12-14].Therefore, the concentration of polymer in the produced liquid will be much higher than that of crosslinker and stabilizer. It can be seen that when the polymer concentration of the produced liquid is detected, the relationship curve between the absorbance value of polymer solution and the polymer concentration should be selected, and the relationship between the absorbance value of polymer gel and the polymer concentration is not suitable.

2.3 Polymer concentration detection and error analysis of produced liquid

Gel flooding technology can reduce the permeability of high osmotic layer, change the flow direction of the subsequent fluid, increase the sweep volume and enhance the oil recovery. The dynamic monitoring of polymer concentration in produced liquid is an important index to guide production and dynamic analysis and adjustment in the process of gel flooding in an oil production plant in Daqing oilfield. Randomly selected 16 oil wells in the gel test area of an oil production plant in Daqing oilfield. The polymer concentration of produced liquid was detected by starch iodide cadmium method and nitrogen determination method respectively.

The relationship between the absorbance value of polymer solution and polymer concentration was taken as the standard curve, and the polymer concentration of produced liquid on November 25, 2015 and December 8, 2015 was detected by starch cadmium iodide method. The results are shown in Table 3.

Table 3 Detection results of polymer concentration in produced liquid (starch cadmium iodide method)

Project / Serial number	Sampling（mL）	2015.11.25 light absorption value	2015.11.25 Polymer concentration（mg/L）	2015.12.8 light absorption value	2015.12.8 Polymer concentration（mg/L）
1	1.2	0.231	15.10	0.245	16.02
2	0.2	0.397	156.05	0.353	138.74
3	1.2	0.111	7.25	0.168	10.97
4	0.4	0.297	58.33	0.338	66.39
5	0.1	0.143	112.42	0.153	120.27
6	0.8	0.258	25.35	0.275	27.01
7	2.0	0.211	8.28	0.288	11.29
8	1.2	0.065	4.23	0.164	10.73
9	1.5	0.475	24.89	0.481	25.16
10	3.0	0.388	10.15	0.457	11.97
11	3.0	0.413	10.82	0.521	13.64
12	0.4	0.394	77.25	0.476	93.41
13	1.6	0.246	12.06	0.299	14.67
14	1.8	0.671	29.28	0.708	30.88
15	2.6	0.215	6.50	0.362	10.92
16	2.0	0.538	21.12	0.554	21.76

The relationship between total nitrogen content of polymer solution and polymer concentration was taken as the standard curve, and the polymer concentration of produced liquid on November 25th 2015 was detected by nitrogen determination method. The results are shown in Table 4.

Table 4 Detection results of polymer concentration in produced liquid (nitrogen determination method)

project / Serial number	2015.11.25（detection result） Total nitrogen（mg/L）	2015.11.25（detection result） Polymer concentration（mg/L）	2015.12.8（Fitting results） Polymer concentration（mg/L）	2015.12.8（Fitting results） Relative error（%）
1	7	15.95	15.83	1.20
2	63	143.55	140.45	1.22

3	5	11.39	11.43	4.02
4	26	59.24	69.39	4.32
5	46	104.82	118.58	1.43
6	10	22.79	26.43	2.19
7	5	11.39	11.34	0.44
8	5	11.39	10.32	3.97
9	11	25.07	24.64	2.11
10	5	11.39	12.44	3.78
11	5	11.39	13.19	3.41
12	33	75.20	95.54	2.23
13	6	13.67	14.18	3.46
14	12	27.34	31.22	1.09
15	5	11.39	11.19	2.41
16	8	18.23	21.17	2.79

At present, starch cadmium iodide method is commonly used to detect polymer concentration in oil field, but the relative error of this method is large. The detection error of nitrogen determination method is small, but its application is seriously limited due to the need of special instruments and expensive equipment in the process of operation. Therefore, by fitting the empirical formula with the polymer concentration detection data in tables 3 and 4, and substituting the detection data of starch cadmium iodide into the formula, the fitting concentration value of nitrogen determination method can be calculated. The polymer concentrations of 16 wells measured by starch cadmium iodide method and nitrogen determination method on November 25, 2015 are plotted in the same coordinate system, as shown in Fig. 5.

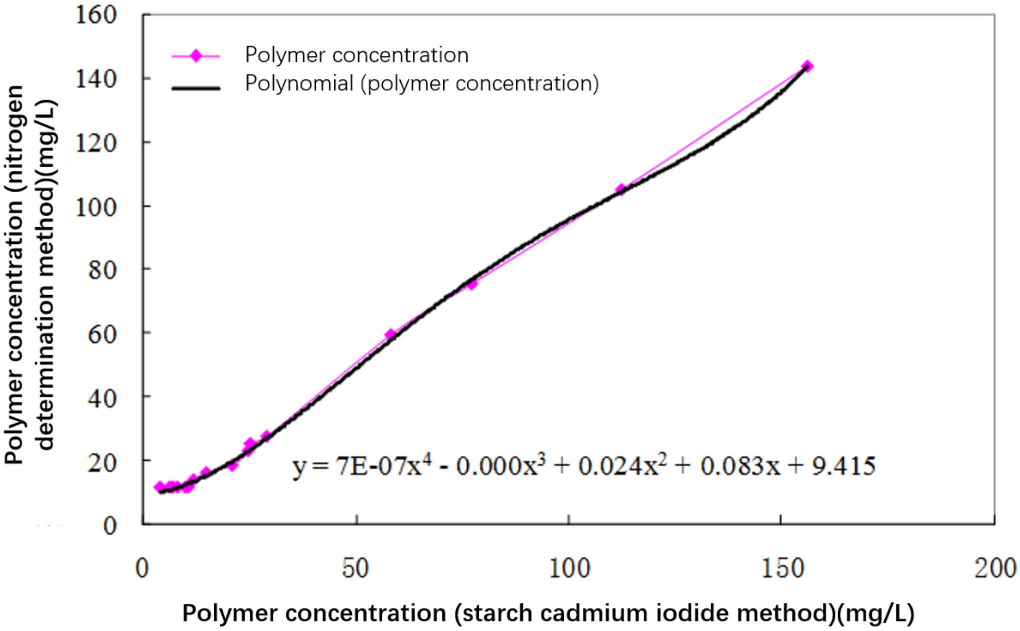


Fig. 5 Polymer concentration curve

It can be seen from Fig. 5 that there is a good linear relationship between the polymer concentration measured by starch cadmium iodide method and nitrogen determination method, and the fitting formula is as follows: $y = 7\times10^{-7}x^{4} - 0.0002x^{3} + 0.0241x^{2} + 0.083x + 9.4152$. Substituting the starch cadmium iodide detection data on December 8, 2015 in Table 3 into the above formula, the fitting concentration value of nitrogen determination method can be calculated (see the fitting results in Table 4). Compared with the data of starch cadmium iodide method, the maximum error is less than 5%.

III. CONCLUSION

（1）When the polymer concentration is the same, the absorbance value of polymer gel is larger than that of polymer solution, and the difference increases with polymer concentration. It can be seen that a certain substance (crosslinking agent or stabilizer) in polymer gel increases the absorbance value.

（2）Core displacement experiments show that crosslinking agents and stabilizers in polymer gel will lose a lot in rock core, resulting in low concentration of retained liquid and negligible influence on absorbance value. It is suggested that the absorbance value of the produced liquid should be used to calculate the polymer concentration with the standard curve of polymer solution when detecting the polymer concentration in the produced liquid.

（3）For the same produced liquid sample, there is a good linear relationship between the polymer concentration measured by starch cadmium iodide method and nitrogen determination method: $y = 7\times10^{-7}x^4 - 0.0002x^3 + 0.0241x^2 + 0.083x + 9.4152$.The fitting concentration value of nitrogen determination method calculated by the above formula was compared with that of starch cadmium iodide method. The maximum value was less than 5%, which verified the correctness of the above formula.

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