

CHELATING ION EXCHANGERS - THE SYNTHESIS AND USES OF POLY(HYDROXAMIC ACID) RESINS

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Abstract - The metal chelating properties of poly(hydroxamic acid) ion exchange resins are described and the synthesis of a macroporous, microbead resin is given. The stability of the resin towards attack by acid solutions is investigated as are several separations involving uranium. Poly(hydroxamic acid) resin columns are able to strip titanium, zirconium, vanadium, molybdenum and bismuth from uranium solutions in nitric acid, the resins will sorb uranium from solutions in the pH range 3 to 4 and purified uranium may be obtained by selective desorption with sodium carbonate solution. The suitability of the resins for sorbing uranium from magnesium bicarbonate solutions, as produced in the Magnox Process, is established as is the effectiveness of the resins for the sorption of uranium from sea-water.

INTRODUCTION

Initial attempts to prepare a poly(hydroxamic acid) chelating exchange resin involved the conversion of conventional weak cation exchangers to acid chlorides followed by reaction with hydroxylamine (Ref. 1, 2 and 3). In fact, very poor conversions of carboxylic acid to acid chloride are obtained for this class of material (Ref. 4), and the resulting polymers contain a high percentage of carboxylic acid groups. Kern and Schultz (Ref. 5) converted a linear poly(methyl methacrylate) to a poly(hydroxamic acid), PHA, with 80 per cent efficiency and found that Fe(III), Cu(II), Ag(I), Zn(II), Hg(II), Al(III), Pb(II) and TiO(II) gave precipitates with the polymeric ligand. Schouteden (Ref. 6) converted poly(acrylonitrile) to PHA by reaction with hydroxylamine in dimethylformamide and Marshal (Ref. 7), using a one-stage synchronous reaction involving sodium hydroxide and hydroxylamine solutions, converted poly(acrylonitrile) fibres to a chelating exchanger having capacities of 1.3 and 5 mmol g⁻¹ for Fe(III) and Cu(II), respectively.

Vernon and Eccles (Ref. 8) prepared a cross-linked PHA ion exchanger by polymerising an acrylonitrile-divinylbenzene mixture, subjecting the resulting granular polymer to hydrolysis in 50 per cent sulphuric acid and reacting the polyamide produced with hydroxylamine solution. The properties of this resin are shown in Table 1(a) and Fig. 1. In column work, the resin was used to separate Fe(III) from Cu(II) and both of these metals from Co(II) and Ni(II). In addition, Fe(III) and U(VI) recoveries from sea-water were carried out with 97-99 per cent efficiencies. Kyffin (Ref. 9) optimised the conditions for cross-linked PHA synthesis, introducing a one-stage hydrolysis-oximation of the acrylonitrile polymer by hydroxylamine solution, and studied the resin capacities for several metal ions over a range of pH values.

Properties of the resin are given in Table 1(b).

Several resin applications were studied, particularly the use of PHA in extracting trace metals from sea-water and from wet ashed sea-weed samples.

A commercial ion exchange resin having amidoxime group functionality is Duolite CS-346 (Diamond Shamrock Co.). Vernon and Kyffin (Ref. 10) used this resin to separate Fe(III), Cu(II) and U(VI), demonstrating that quantitative recoveries of uranium were possible by selective desorption of the element with sodium carbonate solution. Kyffin (Ref. 9) prepared amidoxime polymers and found that these, and Duolite CS-346, were converted to PHA resins when in contact with acid solutions.

Wan Yunus (Ref. 11) studied PHA resin preparation and succeeded in producing a cross-linked PHA exchanger in the form of a macroporous microbead. Metal capacities were high and the kinetics of metal ion exchange were much improved by comparison with the earlier PHA resin granules. It was found that in order to prepare a microbead form of the resin, an acrylonitrile-ethyl acrylate-DVB mixture had to be polymerised. The optimum ethyl acrylate content

TABLE 1. Properties of the various poly(hydroxamic acid) resins produced (a) by Eccles, (b) by Kyffin, (c) by Wan Yunus

	(a)	(b)	(c)
Form	granular	granular	macroporous microbead
Cross-linking (%)	5	5	5
Particle size (μm)	250-750	375-1500	150-300
Water regain (g g^{-1})	1.7	1.1	2.1
Total capacities (mmol g^{-1})			
Fe(III) at pH 3	1.3	1.7	3.5
Cu at pH 4		2.1	3.0
Cu at pH 6	3.2		
U at pH 4			2.9
U at pH 5	1.3	1.2	
Kinetics, $t_{\frac{1}{2}}$ for Cu (min)	43	102	8

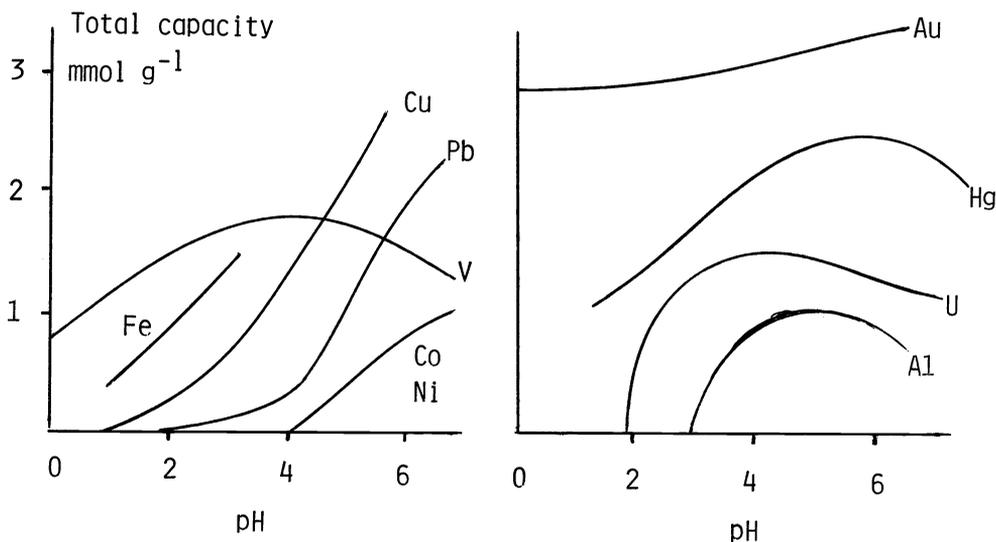


Fig. 1. Capacity vs. pH contours for PHA resin.

of the monomer mix was 20 per cent and the degree of cross-linking 5 per cent. Toluene and hexan-2-one were the solvents added to produce the macroporous structure. Wan Yunus evaluated the resin in terms of its ability to remove uranium from sea-water, obtaining efficient extractions with short sea-water to resin contact times of the order of 5 min. Vernon and Wan Yunus (Ref. 12) evaluated columns of the PHA resin for the recoveries of silver and gold at trace levels and found quantitative recovery of silver from neutral solutions whereas gold was recovered from neutral and acid solutions of up to 1M acid concentration. A silver and gold separation was achieved by selective desorption of silver with 0.5M nitric acid. Gold is strongly bound to the resin and may only be quantitatively removed by the use of potassium cyanide as eluant.

Wan Yunus (Ref. 11) and Noichaya (Ref. 13) have studied the sorption properties of the PHA resin with many metals. It is possible to separate Fe(III) and Al(III) from Ca and Mg and from each other by passing buffered solutions of the metals through exchanger columns. Fe(III) is sorbed at pH 1.5, Al(III) at pH 4 whilst Ca and Mg are not sorbed below pH 7. The known ion exchange properties of the PHA resin are summarised in Table 2.

It is known (Ref. 4 and 13) that many metals such as Fe(III), Ti, Zr, V, Mo form very stable complexes with hydroxamic acids and are capable of being sorbed from acid solutions by PHA. Uranium demonstrates no significant sorption below pH 2 so the possibility of stripping such

metals from acidic uranium containing solutions exists. The uranium may be sorbed at pH 3 leaving metals such as Co, Ni, Pb, Mn, Zn, etc., in solution giving separation from these elements. Finally, uranium may be quantitatively desorbed by a sodium carbonate eluant thus further separating it from species incapable of forming soluble carbonate complexes. The separation of uranium from other species by selective sorption and desorption techniques, together with the method of manufacture of the optimized form of PHA resin and its stability are the subjects of this paper.

EXPERIMENTAL

PHA resin synthesis

Place 500 ml distilled water, 30g anhydrous sodium sulphate, 5g calcium carbonate, 20 ml of a 2 per cent gelatine solution in water, 20 ml hexan-2-one, and 60 ml toluene in a 1 l three-necked flask fitted with reflux condenser, stirrer and thermometer. With stirring, add a mixture of 10 ml 50% divinylbenzene solution in styrene, 20 ml ethyl acrylate, 95 ml acrylonitrile and 1g benzoyl peroxide. Raise the temperature of the stirred solution to 65°C over a period of 1 h and maintain at this temperature for a further 3 h. Heat to 72°C for 1 h, and finally to 85°C for 1 h. Cool and filter the copolymer, washing with hot water, methanol, 1M hydrochloric acid, and again with water until chloride-free.

Place 10g of the copolymer in a 250 ml three-necked flask fitted with stirrer, thermometer and reflux condenser. Add a solution of 6g sodium hydroxide dissolved in 10 ml water, and 10.4g hydroxylammonium chloride dissolved in 100 ml methanol. Stir at room temperature for 12 h then heat to 65°C for 2 h and finally reflux for 15 min. Filter the PHA resin, wash with water, 1M hydrochloric acid and finally with water until chloride-free. Store the resin in deionized water.

Resin stability. 10g samples of resin were shaken continuously with pH 4 buffer or various concentrations of hydrochloric or nitric acids by mechanical shaker. Resin samples were withdrawn at regular intervals for the determination of total capacity for copper from pH 4 buffer (Ref. 14) and for nitrogen content.

Removal of trace metals from uranium solutions

The sample solution used to evaluate the efficiency of PHA columns in purifying uranium consisted of a 5 per cent w/v solution of Analar grade uranyl nitrate in 1M nitric acid containing 100 p.p.m. of each of the following:- copper, iron, lead, manganese, bismuth, titanium, zirconium, thorium, vanadium and molybdenum. Two 1.2 cm i.d. glass columns were packed to a depth of 10 cm with PHA. Column 1 was packed in 1M nitric acid and column 2 in pH 3 aqueous solution. A 100 ml aliquot of sample solution was passed through column 1, the column effluent was analysed for all metal contents. A further 100 ml of sample was passed through a newly prepared column 1, and the column washed with 50 ml 1M nitric acid. Combined effluents were adjusted to pH 3 and passed through column 2, which was then washed with 25 ml of deionized water. Column 2 was then eluted using 100 ml 1M sulphuric acid. Effluent and eluate were analysed for metals content. The process was then repeated on new columns, column 2 being eluted with 1M sodium carbonate, effluent and eluate again being analysed. A column flow rate of 1.5 ml min⁻¹ was maintained throughout the experiments.

Separation of uranium from magnesium (Magnox process)

A sample solution 0.05M in magnesium sulphate and 0.1M in sodium bicarbonate contained 10 p.p.m. uranium. 100 ml of this was passed through a 10 cm PHA column preconditioned with sodium bicarbonate solution and washed with water. The uranium content of the effluent was measured (Ref. 15).

Synthetic Magnox solutions. 12.3g of magnesium sulphate was dissolved in water and the magnesium hydroxide precipitated by addition of sodium hydroxide. The precipitate was washed then suspended in 800 ml of water. Carbon dioxide was blown through it until solution was effected and a pH of approximately 7.0 was reached. This solution, upon dilution to 1 l, was made 50 p.p.m. in uranium and was passed through a preconditioned PHA column at 1.5 ml min⁻¹. On the first run, the actual pH of the feedstock was 7.2, on the second the solution was at pH 7.0. The column effluents were analysed for uranium content.

Uranium extraction from sea-water

2 l samples of filtered sea-water which had been stripped by passing through columns of Chelex 100 resin (iminodiacetic acid functionality) were spiked by the addition of uranium to 18 p.p.m. level. The pH was adjusted to 7.5 and a sample passed through a 20 cm column of PHA preconditioned with 3 per cent sodium chloride solution buffered to pH 7.5. Flow rates of 1.2 and 0.6 ml min⁻¹ gave sample to resin contact times of 10 and 20 min, respectively. Columns were washed with water, the sorbed uranium was then eluted using 2M sulphuric acid and eluates analysed for uranium content. A similar sample was prepared from 3 per cent sodium chloride solution which was 140 p.p.m. in sodium carbonate and 15 p.p.m. in uranium. 2 l of this solution was passed through a PHA column at 1.2 ml min⁻¹. Desorption and

measurement of uranium was as before. The process was repeated using two 40 l samples of settled sea-water. The resins had been preconditioned with sodium carbonate to produce the sodium form. After water washing, the samples were passed through the columns at 4 to 5 ml min⁻¹. Due to the differing amounts of resin used (column 1 length 30 cm, column 2 length 50 cm) the sample to resin contact times were 2.5-3 min and 7.5-9 min, respectively. Uranium was eluted and measured as before.

RESULTS AND DISCUSSION

PHA resin synthesis

The PHA resin, prepared as described, is a white, macroporous, microbead polymer giving intense colours on sorption of metals. Thus, a sample containing a few parts per million of iron(III), copper, or uranium, on passing through a PHA column, gives rise to intense red, blue or orange bands, respectively. Total capacities for metals are high, as shown in Table 2, and the kinetics of metal uptake are good. It is seen from Table 1 that the kinetics,

TABLE 2. Total capacities of resin (c) at the optimal pH values

Metal sorbed	Capacity (mmol g ⁻¹)	Optimal pH
Ag	3.2	6
Al	2.9	4
Au	4.3	5
Co	0.4	6
Cu	4.0	5
Fe(III)	3.5	3
Mn(II)	0.5	6
Ni	0.2	6
U(VI)	2.9	4

as determined by the time taken to occupy 50 per cent of available sites by copper, improve as the water regain increases. However, the kinetics also improve as the resin particle size decreases and it is not known which of these two variables has the greater effect upon the kinetics of metal sorption.

An advantage of the PHA resin is that it is prepared from low cost materials and the method of synthesis given produces a consistent material - resin capacity and kinetic properties not varying when resin production is scaled up by a factor of twenty.

Resin stability. The seventy per cent of acrylonitrile present in the initial copolymer may convert to either an amidoxime or a hydroxamic acid group during the oximation reaction, whereas the twenty per cent ethyl acrylate converts only to hydroxamic acid. An acid medium, such as is used for metal desorption, will favour the conversion of amidoxime to hydroxamic acid with the further possibility of very acidic eluants attacking the PHA functionality so bringing about a loss in capacity. Stability towards acids was assessed by prolonged contact of a resin with solutions of various degrees of acidity and the results of these tests are shown in Table 3 in terms of the residual nitrogen content of the resin and its total capacity for copper at pH 4. It is seen that the resin is stable in water and pH 4 buffer but is affected by 0.1M hydrochloric acid, the rate of decomposition of the resin increasing as the acidity increases. After sixty days' continuous contact with 4M hydrochloric acid, the percentage of the original nitrogen remaining in the resin is 61.3. The copper capacity of this material as a percentage of the copper capacity of the original resin is 61.5. However, the PHA resin exhibits fairly high stability in the short term, two hours' contact with 4M hydrochloric acid has no apparent effect on the copper capacity.

If the conversion acrylonitrile to amidoxime is quantitative, the resin should contain 26 per cent nitrogen. If all the amidoxime is hydrolysed to PHA, the nitrogen content should be 14.5 per cent. Therefore, a resin containing 21 per cent nitrogen (the initial value) contains 40 per cent amidoxime and 50 per cent PHA. Table 3 shows that a pH 4 buffer does not cause amidoxime to hydrolyse; in fact, total conversion of amidoxime to PHA takes 45 days in 1M hydrochloric acid. It is only prolonged contact with highly acidic solutions (1M hydrochloric acid for more than 45 days or 4M acid for more than 3 days) which causes loss of

functionality as seen by the nitrogen content falling below 14.5 per cent.

TABLE 3. Stability of PHA resin, showing decrease in (a) nitrogen content and (b) total copper capacity as a function of time in contact with acid solutions. (Initially N 21%, copper capacity 2.6 mmole g⁻¹)

Equilibrating solution	Time of equilibration			
	2 h	3 d	45 d	60 d
	N/cap	N/Cap	N/Cap	N/Cap
Deionized water	2.6	20.9/2.6	20.4/2.7	20.4/2.6
pH 4 buffer	2.7	20.5/2.3	19.9/2.5	19.3/2.6
0.1M HCl	2.6	19.3/2.2	16.1/2.3	15.4/2.0
1M HCl	2.6	18.5/1.8	14.3/1.6	13.9/1.6
4M HCl	2.5	17.2/1.5	12.6/1.8	12.5/1.6

Hydroxamic acids may be destroyed by oxidation so the stability of PHA towards various concentrations of nitric acid was investigated. Figure 2 shows the decrease in copper capacity as a function of time of shaking of resin with acid. The resin shows poor stability towards nitric acid, losing 50 per cent of its functional groups in 4 days' contact with 1M nitric or 39 per cent loss after 7 days with 0.5M nitric acid.

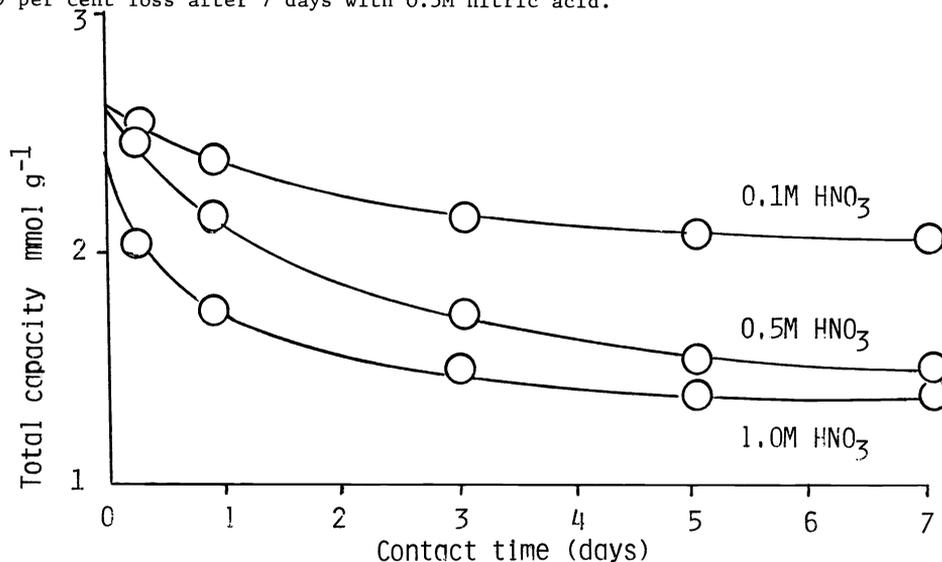


Fig. 2. Stability of PHA resin to prolonged contact with nitric acid in terms of resin capacity for copper.

Metal separations

The selective removal of metals such as iron, titanium, vanadium, zirconium and molybdenum from uranium solutions is effected by ion exchange of these species from dilute nitric acid when uranium is not sorbed by the resin. The column effluent is then raised to pH 3 and passed through a second column where uranium is sorbed together with copper and traces of lead, manganese, bismuth and thorium. Table 4 gives the resin capacities for metals from 1M nitric acid and from pH 3 buffer.

The uranium may be completely desorbed from the PHA column using either 1M sulphuric acid or 1M sodium carbonate as eluant. Solutions containing 5 per cent uranyl nitrate in 1M nitric acid, and containing 10 mg of each metal added as impurity, were processed by the two-column technique, and desorption by sulphuric acid or sodium carbonate used to recover the uranium. Table 5 shows the effectiveness of this treatment for the removal of trace metals from uranium. Elution with sulphuric acid leaves the uranium contaminated by thorium, iron, copper, lead and manganese, the process being very effective for the removal of titanium, vanadium, molybdenum, zirconium and bismuth. Elution with sodium carbonate, although giving a slightly lower uranium recovery, gives a much cleaner product. Thorium, molybdenum and

TABLE 4. Total capacities of PHA resin from 1M nitric acid and from pH 3 buffer

Metal sorbed	Total capacity (mmol g ⁻¹)	
	1M HNO ₃	pH 3 buffer
Cu(II)	0	1.7
Fe(III)	0.1	3.5
Ti(IV)	0.9	0.7
Mo(VI)	0.8	1.2
V(V)	1.3	1.2
Pb(II)	0	0.1
Mn(II)	0	0.1
Bi(III)	0.4	0.5
Th(IV)	0	0.1
U(VI)	0	2.2
Zr(IV)	1.2	0.1

TABLE 5. Removal of trace metals from uranium solutions in 1M nitric acid by ion exchange on PHA followed by sorption of uranium at pH 3 and desorption by 1M sulphuric acid or 1M sodium carbonate

Metal	Percentage of initial metal content in eluate		
	Eluant	1M H ₂ SO ₄	1M Na ₂ CO ₃
U		98.5	93
Mn		58	50
Pb		90	0
Cu		94	0.6
Fe		68	5
Ti		3	0
Mo		2	29
V		7	1
Th		24	25
Bi		0	0
Zr		0	0

manganese are the only serious contaminants in this system. Table 6 shows the percentage of the metals passing through column 1 (feedstock in 1M nitric acid) and present in the pH 3 feedstock to column 2. This stage is particularly effective for zirconium removal, whilst the majority of the titanium, molybdenum, vanadium and bismuth are also removed.

TABLE 6. Removal of trace metals from uranium in 1M nitric acid on passing through a PHA column

Metal	U	Mn	Pb	Cu	Fe	Ti	Mo	V	Th	Bi	Zr
Percentage of metal in effluent	100	75	100	100	83	20	33	29	100	30	2

Separation of uranium from magnesium

In the Magnox process, magnesium is solubilized as the bicarbonate by blowing carbon dioxide through a suspension. Under these conditions, traces of uranium present form the soluble tricarbonato complex. PHA resin is able to sorb uranium from this solution if the pH is around 7. This can be achieved by ensuring that the solution is saturated with carbon dioxide. Below pH 7.5, PHA resins show no affinity for magnesium although by pH 9, the magnesium capacity of the resin is 1.0 millimole/g.

By pH control of the feedstock it is possible, therefore, to strip uranium from Magnox solutions. Table 7 gives the working pH and percentage removal of uranium from such solutions.

TABLE 7. Sorption of uranium from Magnox solutions (magnesium bicarbonate containing traces of uranium) by ion exchange on PHA

System	pH	Uranium in feedstock ($\mu\text{g ml}^{-1}$)	Percentage U removed
0.05M MgSO_4 0.1M NaHCO_3	7.4	10	80
Magnox solution $\text{Mg}(\text{HCO}_3)_2\text{-CO}_2$	7.2	50	96.5
Magnox solution $\text{Mg}(\text{HCO}_3)_2\text{-CO}_2$	7.0	50	99.9

Recovery of uranium from sea-water

Kyffin (Ref. 9) carried out recovery tests for uranium with PHA. Passing 300 l of sea-water through a resin column and allowing a resin to sea-water contact time of 5 min, he found that 37 per cent of the uranium present was retained by the column.

Although the total capacity of the microbead resin for uranium is 2.9 millimole/g at the optimal pH 4, the capacity then falls as the pH increases and, for sea-water, pH 7.8 where the uranium is present as the tricarbonato complex, the resin capacity is 0.9 millimole/g. This figure is derived from equilibration studies using 0.5M sodium chloride solution containing 10 millimolar uranium and sufficient sodium carbonate to produce the tricarbonato complex. It represents the maximum resin loading which could be achieved from sea-water. Table 8 shows the recoveries of uranium from spiked sea-water samples and from a 3 per cent

TABLE 8. (a) Extraction of uranium from sea-water spiked with uranium and from 3% sodium chloride solution, (b) from 40 l sea-water samples by ion exchange on a PHA column.

Sample	U extracted (mg)	Percentage U extracted	Contact time (min)
a) Spiked sea-water	16.2	46	10
Spiked sea-water	21.0	60	20
3% NaCl solution	24.3	81	10
b) 40 l sea-water	91 (μg)	76	3
40 l sea-water	106 (μg)	88	8

sodium chloride solution containing the uranium tricarbonato complex as a function of resin to sample contact time; these indicate that a contact time of 10-20 min is necessary for 50 per cent uranium recovery. The results in Table 8(a), however, were obtained using a column of PHA in the hydrogen form. It was subsequently shown that the kinetics of uranium uptake from sea-water are significantly enhanced if the resin is in the sodium form. Table 8(b) shows recoveries from sea-water samples of 76 per cent and 88 per cent for contact times of 3 and 8 min, respectively, and suggest that PHA resin may be the best ion exchanger for the solution of this problem.

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