Modelling Synergistic Solvent Extraction of Nickel and Cobalt

Mike Dry

Arithmetek Inc.

Abstract

While McCabe-Thiele plots are useful for designing single-component solvent extraction systems, not least because of their simplicity, they are less useful for multi-component solvent extraction.

This paper presents a relatively simple method, compared to other approaches, for modelling solvent extraction as chemical equilibrium reactions between the various aqueous and organic species. The essence of this approach is how values for the equilibrium constants can be extracted from standard laboratory data. Synergistic solvent extraction of nickel is used to illustrate the method.

Introduction

Solvent extraction has been well described elsewhere [1]. It entails chemical equilibrium, or an approach to equilibrium, between the aqueous and organic phases. Designing the solvent extraction portion of a process requires quantitative knowledge of the relevant equilibrium chemistry. Typically, in the absence of data from continuous operation, be that mini-plant, pilot plant or full commercial scale, the available information comes from laboratory shake-out tests in which the initial volumetric ratio of the organic to the aqueous phase is varied, the phases are contacted for a time long enough to equilibrate them and then separated and analysed. In some cases, the pH of the system is adjusted with appropriate base or acid. The resulting information is commonly presented as curves of extraction versus pH or as isotherms plotting the equilibrium concentration of an element of interest in the organic phase against the corresponding concentration in the aqueous phase (the McCabe-Thiele plot).

While the use of McCabe-Thiele plots for the individual elements of interest is convenient for establishing preliminary process designs, particularly when only one element (e.g. copper) enters the organic phase, when more than one element can enter the organic phase the elements concerned compete for the organic reagent, violating a crucial assumption in the McCabe-Thiele plot, i.e. that the equilibrium can be accurately represented by a two-dimensional graph. Since many solvent extraction systems entail more than one element that can enter the organic phase, a computational approach that accounts for competition between the elements of interest for the organic reagent would clearly be a useful tool for the preliminary extrapolation of data from laboratory shake-out tests to an initial process design.

Example

The example chosen for this paper is the synergistic solvent extraction of nickel and cobalt from a typical laterite leach liquor. In synergistic solvent extraction (SSX), the organic phase contains two reagents, one termed the extractant and the other the synergist. SSX can use combinations of acidic and neutral, two acidic, two neutral, anionic and neutral, cationic and anionic or two anionic extractants [2].

To illustrate the effect of adding the synergist, Figure 1 shows isotherms for an extractant (Versatic 10) on its own and for that extractant plus a synergist referred to only as Nicksyn [1].

Note the significantly improved separation between nickel and cobalt, and also between cobalt and manganese, in the system using the extractant plus synergist.
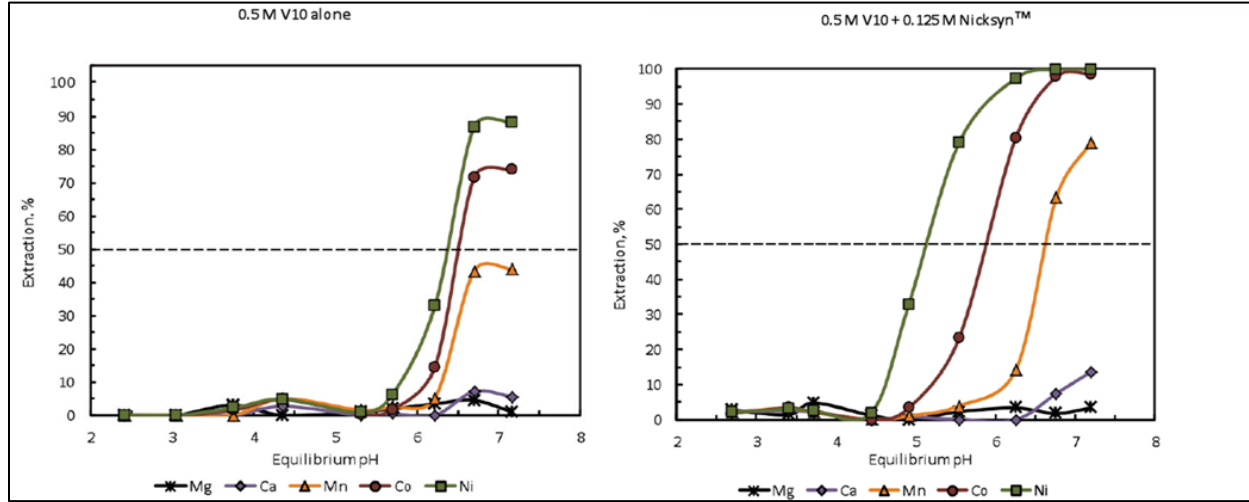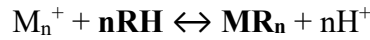

Figure 1- Impact of the synergist [3]

Theory

In conventional solvent extraction, the equilibrium between the aqueous and organic phases can be depicted as follows for each element of interest, R being the extractant, the species shown in bold being in the organic phase and the others in the aqueous phase:

$$M_n^+ + \mathbf{nRH} \leftrightarrow \mathbf{MR_n} + nH^+$$

The associated equilibrium reaction is then expressed in terms of an equilibrium constant K for each such reaction:

$$K = \frac{[\mathbf{MR_n}][H^+]^n}{[M^{n+}][\mathbf{RH}]^n}$$

Here, the square brackets denote concentration in the relevant phase. Strictly, that should be activity, but concentration is easier to use. The assumption implicit in using concentration is that the activity coefficients of the species concerned do not vary much, or if they do, the variations in the numerator and denominator cancel out. While this is a blatant numerical short-cut, it greatly reduces computational complexity. This is a fairly safe assumption in sulphate systems, but in chloride systems chloro-complexes can make the chemistry appreciably more complex.

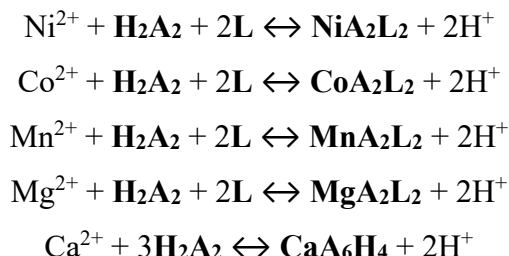In systems containing more than one element that can enter the organic phase, the different equilibrium relationships are linked by the concentrations of H^+ in the aqueous phase and RH in the organic phase. For elements M_1, M_2, etc., this leads to the following linking equations, the subscript *i* denoting the individual elements:

$$\sum M_i R_n = nRH_{input}$$

$$H^+ = \sum x_i n_i M_i^{n+}$$

Thus, given the relevant equilibrium constants, for any given number of elements taking part in the aqueous-organic equilibrium, a set of equations can be defined for the distributions of the individual elements between the aqueous and organic phases.

The theory is similar for synergistic solvent extraction, with the equilibrium reactions adapted to accommodate the extractant and the synergist. In the system shown in Figure 2, the aqueous-organic equilibrium reactions are [3]:

$$Ni^{2+} + \mathbf{H_2A_2} + \mathbf{2L} \leftrightarrow \mathbf{NiA_2L_2} + 2H^+$$

$$Co^{2+} + \mathbf{H_2A_2} + \mathbf{2L} \leftrightarrow \mathbf{CoA_2L_2} + 2H^+$$

$$Mn^{2+} + \mathbf{H_2A_2} + \mathbf{2L} \leftrightarrow \mathbf{MnA_2L_2} + 2H^+$$

$$Mg^{2+} + \mathbf{H_2A_2} + \mathbf{2L} \leftrightarrow \mathbf{MgA_2L_2} + 2H^+$$

$$Ca^{2+} + 3\mathbf{H_2A_2} \leftrightarrow \mathbf{CaA_6H_4} + 2H^+$$

Here the species H_2A_2 and L are the extractant and synergist, respectively. There is also an equilibrium between the extractant and the synergist:

$$\mathbf{H_2A_2 + 2L \leftrightarrow 2HA \bullet L}$$

The set of equations for synergistic solvent extraction has this extra equilibrium between the extractant and the synergist, linking these species.

Modelling

Modelling the chemistry of the above example of synergistic solvent extraction requires, first, finding values for the various equilibrium constants from the data shown in the right-hand graph in Figure 1. Table 1 lists the composition of the aqueous feed and the composition of the starting organic phase. The experiments were done at 25°C, and the volumetric ratio of organic to aqueous phases was 0.45:1. Table 2 lists the extractions measured at varying pH values. Table 3 lists the concentrations of nickel and cobalt in the organic and aqueous phases at equilibrium, at a pH value of 5.8 and varying O:A ratios. Note that the concentrations of the active reagents are given in mol/L rather than the more normal volume percent, since this is how they were given in the reference [1].

Table 1 – Aqueous feed and starting organic phase compositions [3]

Aqueous feed, g/L					Organic, mol/L	
Ni^{2+}	Co^{2+}	Mn^{2+}	Mg^{2+}	Ca^{2+}	H_2A_2	L
3	0.5	0.66	20.2	0.46	0.25	0.5

In terms of numerical modelling of the system, the challenge is to find a set of values for the various equilibrium constants that enables sufficiently accurate reproduction of the measured data. One way in which this can be done is via spreadsheet calculations using the initial and final compositions of the aqueous and organic phases at each value of pH tested. The initial phase concentrations and the measured extractions can also be used to calculate the composition of each phase after contact and phase separation. Table 4 and Table 5 show the results of these calculations for the data in Table 2, assuming negligible change in the density of the aqueous and organic phases. The calculations are similar for the data in Table 3.

Table 2 – Measured extractions [3], (O:A = 0.45)

pH	Measured extraction, %				
	Ni²⁺	Co²⁺	Mn²⁺	Mg²⁺	Ca²⁺
2.7	0.4	0.0	0.0	0.0	0.0
3.2	1.8	2.1	0.0	0.0	0.0
3.9	2.9	1.4	0.0	0.0	0.0
4.4	18.2	3.6	0.0	0.0	0.0
4.9	76.1	14.3	0.0	0.0	0.0
5.7	98.2	75.0	3.6	0.0	0.0
6.4	99.6	97.9	27.9	0.0	0.0
6.7	100	99.3	78.6	0.0	4.3
7.3	100	100	95.7	3.6	15.0

Table 3 – Measured nickel and cobalt isotherm data [3] at pH 5.8

Nickel, mg/L		Cobalt, mg/L	
Org	Aq	Org	Aq
413	31	50	1
723	38	81	4
2890	76	315	73
5574	183	403	214
10219	1910	153	469
9703	2461	112	469
7892	2436		

The final concentration cannot be calculated directly for the complex between the extractant and the synergist, HA•L, therefore the final concentrations of H₂A₂ and L can also not be calculated directly. Were the concentrations for H₂A₂ and L known, the various equilibrium constants could be calculated from them and the numbers in Table 4 and Table 5.

A convenient approximation for the concentration of protons uses the measured pH:

$$[H^+] = 10^{-pH}$$

Taking nickel as an example, the equilibrium constant can be calculated using the following equation:

$$K_{Ni} = \frac{[NiA_2L_2][10^{-pH}]^2}{[Ni^{2+}][H_2A_2][L]^2}$$

The equilibrium constant for the complex formed by the extractant and the synergist is:

$$K_{HA \bullet L} = \frac{[HA \bullet L]^2}{[H_2A_2][L]^2}$$

Table 4 – Equilibrium data, aqueous phase, mol/L

pH	Ni^{2+}	Co^{2+}	Mn^{2+}	Mg^{2+}	Ca^{2+}
2.7	0.0509	0.0085	0.0120	0.8311	0.0112
3.2	0.0502	0.0083	0.0120	0.8311	0.0111
3.9	0.0497	0.0084	0.0120	0.8311	0.0110
4.4	0.0418	0.0082	0.0120	0.8311	0.0110
4.9	0.0122	0.0073	0.0120	0.8311	0.0109
5.7	0.0009	0.0021	0.0116	0.8311	0.0108
6.4	0.0002	0.0002	0.0087	0.8311	0.0107
6.7	0.0001	0.0001	0.0026	0.8311	0.0110
7.3	0.0000	0.0000	0.0005	0.8014	0.0098

Table 5 – Equilibrium data, organic phase, mol/L

NiA$_2$L$_2$	CoA$_2$L$_2$	MnA$_2$L$_2$	MgA$_2$L$_2$	CaA$_6$H$_4$
0.0004	0.0000	0.0000	0.0000	0.0007
0.0020	0.0002	0.0000	0.0000	0.0008
0.0032	0.0001	0.0000	0.0000	0.0010
0.0207	0.0003	0.0000	0.0000	0.0011
0.0864	0.0012	0.0000	0.0000	0.0013
0.1116	0.0064	0.0010	0.0000	0.0014
0.1132	0.0083	0.0074	0.0000	0.0016
0.1133	0.0084	0.0210	0.0000	0.0011
0.1135	0.0085	0.0256	0.0292	0.0038

For arbitrary values for the concentrations of HA•L at the various values of pH, stoichiometry gives values for the concentrations of H$_2$A$_2$ and L, and corresponding values can be calculated for the values of the equilibrium constants K at the different values of pH. Were all the concentrations of HA•L, and thus also the concentrations of H$_2$A$_2$ and L, correct, all the calculated values for any given equilibrium constant would be the same for all the values of pH for which it is calculated. The problem, then, is reduced to finding the concentration of HA•L at each measured value of pH, such that the spread in the calculated values of the individual equilibrium constants is minimised.

One way of doing this is to set up a spreadsheet using the final concentrations of the relevant species in the aqueous and organic phases for each measurement, initially assuming arbitrary concentrations of HA•L and using the resulting numbers to calculate values for the individual equilibrium constant at each value of pH. The values of any given equilibrium constant will, of course, not all be the same at the different values of pH. Next, any suitable iterative calculation engine (like the Solver add-in in Microsoft's Excel) can be used to search for a set of HA•L concentrations that minimises the standard deviation around the average of the values calculated for the individual constants, including the equilibrium constant for HA•L. The results of this exercise are listed in Table 6. The rows at pH values of 3.2 to 7.3 are from the data in Table 2 and the rows at pH 5.8 are from the data in Table 3.

To establish whether or not this approach has any merit, the system was simulated using commercially available flowsheet simulation software known as AspenPlus®, as a single stage of contact between the aqueous and organic phases as listed in Table 1, with the pH adjusted to between 2.7 and about 7.6. Figure 2 shows the results of this exercise. The symbols are the data and the lines are the model predictions. While not perfect, the fit of model to data would appear to be reasonably good.

Table 6 – Equilibrium constants, expressed as LnK

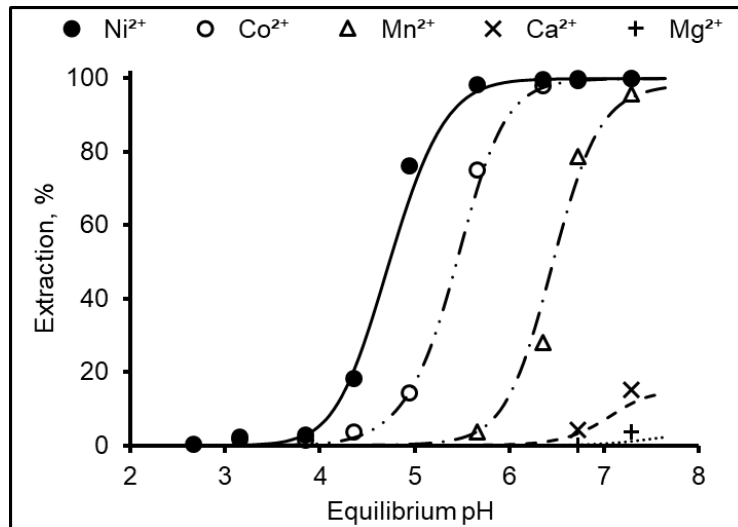| pH	Ni	Co	Mn	Mg	Ca	HA•L
3.9	-14.2	-15.7				4.09
4.4	-14.0	-16.6				4.47
4.9	-13.4	-17.2				4.35
5.7	-13.4	-17.1				4.25
6.4	-14.0	-16.6	-20.6			5.36
6.7			-20.6		-23.4	4.29
7.3				-27.9	-23.4	3.75
5.8	-14.0					8.41
5.8	-14.0					8.06
5.8	-14.1	-16.3				6.70
5.8	-13.9	-16.6				6.59
5.8	-13.8	-16.6				6.88
Std. Dev.	0.4	0.6	0.0		0.0	0.46
Average	-14.0	-16.5	-20.6	-27.9	-23.429	4.36
			Sum of standard deviations, minimised			1.40

Figure 2 – Measured[3] and predicted extractions versus pH

In the published work [3] used in this exercise, extraction isotherms were generated for nickel and cobalt by means of a sequence of batch contacts at different O:A ratios, using the same aqueous and organic feed compositions (Table 1) as were used to generate the curves in Figure 2, except that aluminium (0.2 g/L Al^{3+}) was added to the aqueous feed to evaluate the effect of

incomplete aluminium removal in the upstream part of the circuit. Since a curve of extraction versus pH was not measured for aluminium, a value that caused the model to fit the isotherm for nickel was found by trial and error for the equilibrium constant of the aluminium extraction reaction:

$$Al^{3+} + 1\tfrac{1}{2}H_2A_2 + 3L \leftrightarrow AlH_3A_3L_3 + 3H^+$$

Figure 3 shows the results of this exercise. The symbols are data, the dashed line is the model prediction for nickel assuming no aluminium in the aqueous feed and the solid line is the model prediction for nickel accounting for the aluminium added to the aqueous feed. The dotted line is the model prediction for cobalt. The difference between the predicted isotherms for nickel is due to the aluminium in the feed, which is more strongly extracted than nickel and thus locks up some of the extractant and synergist, reducing the capacity of the organic phase for nickel.
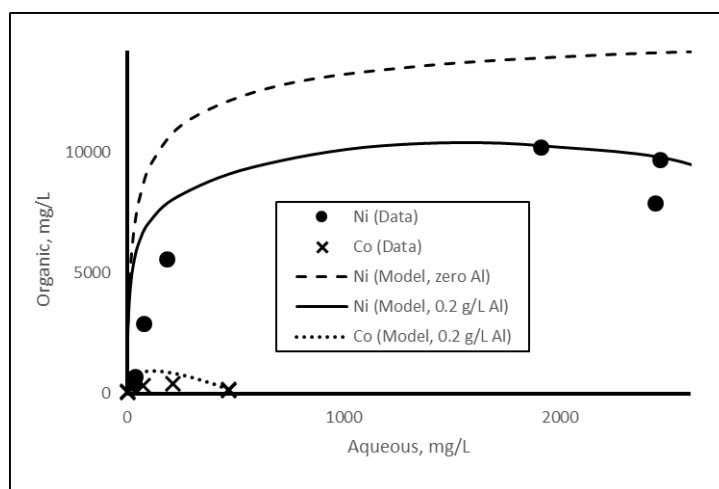

Figure 3 – Measured [3] and predicted isotherms for Ni and Co

Figure 4 shows data (top graph) from a batch-cyclic test campaign simulating a four-stage counter-current extraction sequence alongside the corresponding model predictions (bottom graph). The vertical axes in Figure 4 are logarithmic. In this case, the feed organic phase contained 0.25M H_2A_2 (extractant) and 0.25M L (synergist). The aqueous feed was as listed in Table 1, with 54 mg/L of Al^{3+} added. In the upper two graphs the vertical axes are on the logarithmic scale to better show the levels of Mn, Mg and Ca. In the lower two graphs the vertical axes are on a linear scale to better show the selectivity for nickel over cobalt and even more so against the other elements. The values of the various equilibrium constants in the model were adjusted from those listed in Table 6 to make it fit that data better. Adjusting the parameters of a model as more experimental results become available is a normal part of process development. The fit of model to data is, of course, not perfect, but the model does correctly predict the relative levels of the different elements extracted, certainly sufficiently to make it useful for interpreting early-stage data and planning further work.

Conclusion

It is possible to model the synergistic solvent extraction of multiple elements using aqueous-organic equilibrium reactions and the concentrations in the aqueous and organic phases.

The offering of this paper is the technique used to calculate values for the equilibrium constants from laboratory data.
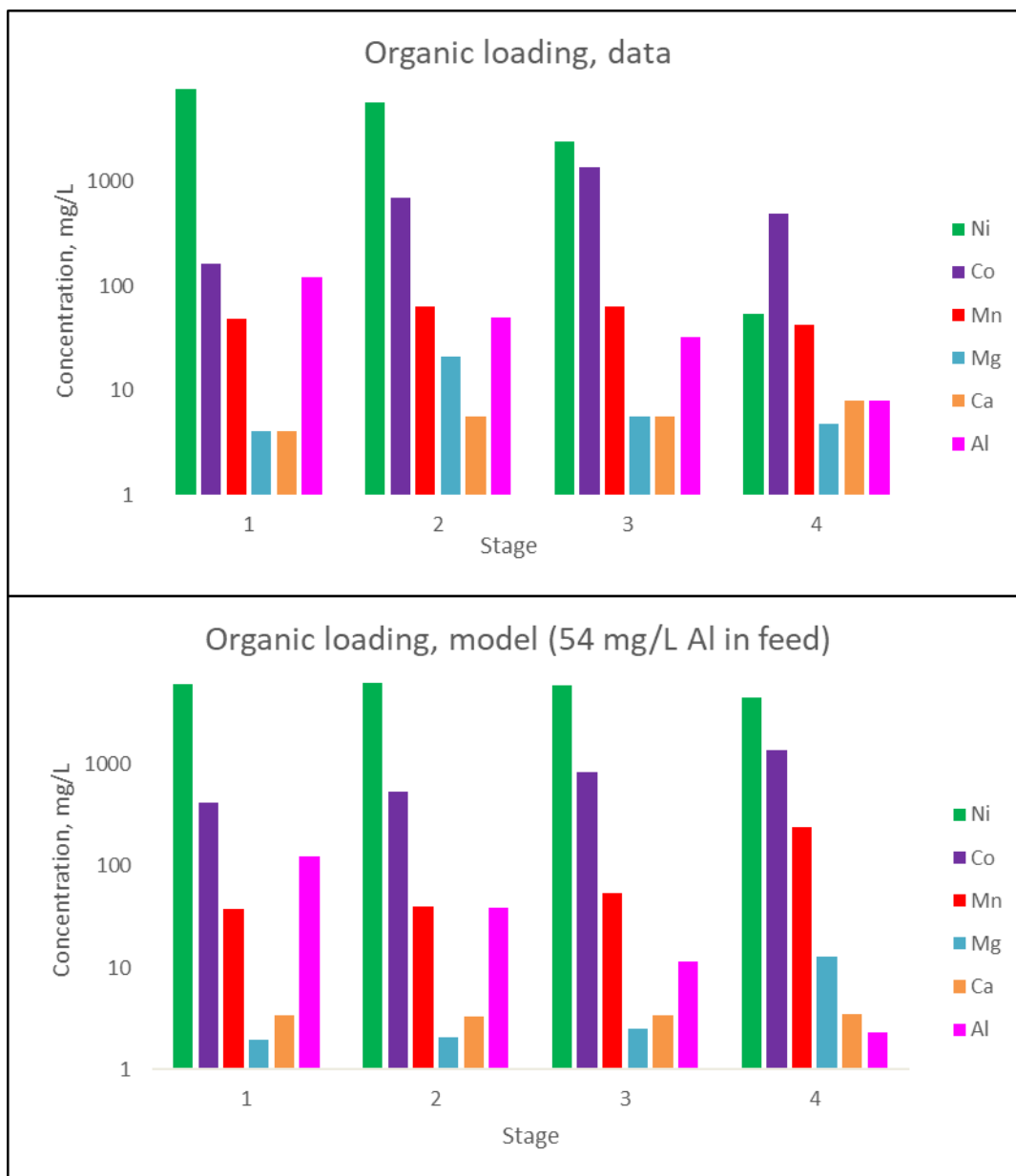

Figure 4 – Organic loading, data from four-stage extraction, batch-cycle testing [3]

Hopefully this paper will encourage others to adopt and refine this approach for modelling multi-component solvent extraction. An obvious avenue for further investigation would be to bring in activity coefficients, thereby removing a major simplifying assumption used in this work, i.e. that concentrations an be used to calculate the relevant equilibria.

One complexity of SSX circuits is that the aqueous solubility of the extractant, while small, is not the same as that of the synergist. That means that the ratio of extractant to synergist can drift over time and operating a circuit using SSX could well require careful monitoring of the organic phase.

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