Efficiency of Brown Stock Pulp washing in Liquid Properties

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Abstract
Washing is simply bulk removal of the liquor surrounding the pulp fibers. In a laboratory washing cell, the mechanism of the displacement washing of unbleached Kraft pulp was investigated. The efficiency of displacement washing depends on the degree of mixing and also on the rate of desorption and diffusion of dissolved solids and chemicals from the pulp fibers. Using the step function input change method, the washing breakthrough curves obtained experimentally were described by the axially dispersed plug flow model. A correlation between Peclet numbers, Kappa numbers the wash yield, and pH of wash liquid was derived as well. The level of sorbed sodium varies with kappa number and pH. The effect of the superficial wash liquid velocity and of the mobility of displacing and displaced liquids upon the axial dispersion coefficient was discussed.
Keywords: Peclet number, Kappa number, pH number

Introduction

The mechanics superimposed by mass transport phenomena like diffusion. Diffusion of black liquor solids inside the fiber voids and the surrounding liquor is dependent on the concentration difference between the black liquor solutes at the inside and at the outside of the fibers and the size of the molecule. Displacement washing is used industrially to remove spent pulping liquor from the pulp [1]. However, the removal of the dissolved solids is never perfect because of molecular and convective diffusion causing mixing between the wash liquid and resident liquor, in homogeneities in the pore structure of the pulp pad, slow diffusion of the solutes from the fibres, and sorption of solutes on the fibres. The ideal case would be a piston-like displacing liquid with no interfacial mixing between the displaced and displacing fluids. It is known that the acid washing can improve the hydrogen peroxide bleaching of Kraft pulps [2-6]. Up to now, however, very little effort has been devoted to the investigation of the effect of acidification on lignin removal from pulp fibres bed [7]. Therefore, the objective of the present study was to investigate the effect of the pH value of wash liquid on the efficiency of displacement washing process. For high initial bed liquor concentrations, the simple axially dispersed plug flow model [8] appeared to be satisfactory for describing the experimental displacement washing breakthrough curves. The basic pulp washing operations are dilution/extraction and displacement washing.

In dilution/extraction washing, the pulp slurry is diluted and mixed with weak wash liquor or clean water. Then the liquor is extracted by thickening the pulp, either by filtering or by pressing. This procedure must be repeated many times in order to sufficiently wash the pulp. The efficiency of dilution/extraction washing depends primarily on the consistencies to which the pulp is diluted and thickened.

In displacement washing, the liquor in the pulp is displaced with weaker wash liquor or clean water. Ideally, no mixing takes place at the interface3 of the two liquors. In practice, however, it is impossible to avoid a certain degree of mixing. Some of the original liquor will remain with the pulp and some of the wash liquor will channel through the pulp mass. The efficiency of displacement washing then depends on this degree of mixing and also on the rate of desorption and diffusion of dissolved solids and chemicals from the pulp fibers.

All pulp washing equipment is based on one or both of these principles. Displacement washing is utilized in a digester washing zone. A rotary vacuum washer utilizes both dilution/extraction and displacement washing, while a series of wash presses utilizes dilution/extraction.

Experimental

The step signal-response experiments were carried out in the cylindrical displacement washing cell with an internal diameter of 35 mm and an adjustable bed height. The fibres bed occupied the volume between the septum and piston, which were made permeable by 64 holes each of 1 mm diameter. Pulp beds were formed from a low consistency suspension of unbeaten unbleached Kraft pulp in black liquor, with the initial concentration of alkali lignin of 70 kg m^{-3}. After compressing to desired thickness of 30 mm, the consistency of oven-dried pulp in bed was approximately 12 mass %. To characterize the softwood pulp fibres, their physical properties were determined as well. The beating degree, which indirectly characterizes the swelling capacity of pulp fibres, of 13 SR was found. The degree of pulp delignification was expressed in terms of kappa number equal to 23.7. The fibres length was measured in the wet state using Kajaani FS 100 instrument. The weighted average length was 2.13 mm, while the numerical average length of 1.25 mm was obtained. The coarseness of fibres had a value of 0.17 mg m^{-1}. The effective specific volume of fibres in a swell state determined according to Ingmanson [9] was 2.69×10^{-3} m^3 kg^{-1} and corresponding specific surface of fibres was 876 m^2 kg^{-1}. Liquids having different pH value were used as wash liquids. The distilled water was acidified to pH value ranging from 2.1 to 6.2 with sulfuric acid, while pH values in alkaline region up to 10.9 were adjusted by the addition of sodium hydroxide. To start the washing experiment, wash liquid maintained at a temperature of 21-23°C was distributed uniformly through the piston to the top of bed, approximating a concentration step change. Samples of the washing effluent were taken at different time intervals until the effluent was colorless. The concentration profile of alkali lignin in the output stream was measured as a function of time by means of an ultraviolet spectrophotometer operating at a wavelength of 295 nm. Washing experiments with distilled water together with determination of the pulp fibres physical properties were described in detail earlier [10].

Result and Discussion

a).**Washing Curves**

Measured breakthrough curves were normalized by plotting them in coordinates of the ratio of the instantaneous outlet to the initial mother liquor concentration in the bed, P_e / P_0, vs. the wash liquor ratio, RW, defined as the ratio of the mass of the wash liquor passed through the bed and the mass of the mother liquor present in the packed bed. A typical example of washing curve is given in Fig. 1, where also the limits of plug flow without diffusion and of infinite diffusion as in ideally stirred vessel are shown. Intrinsic properties of effluent stream leaving the bed are changed during displacement process. At the beginning, in the first portions discharged from the bed the concentration of original mother liquor was measured.

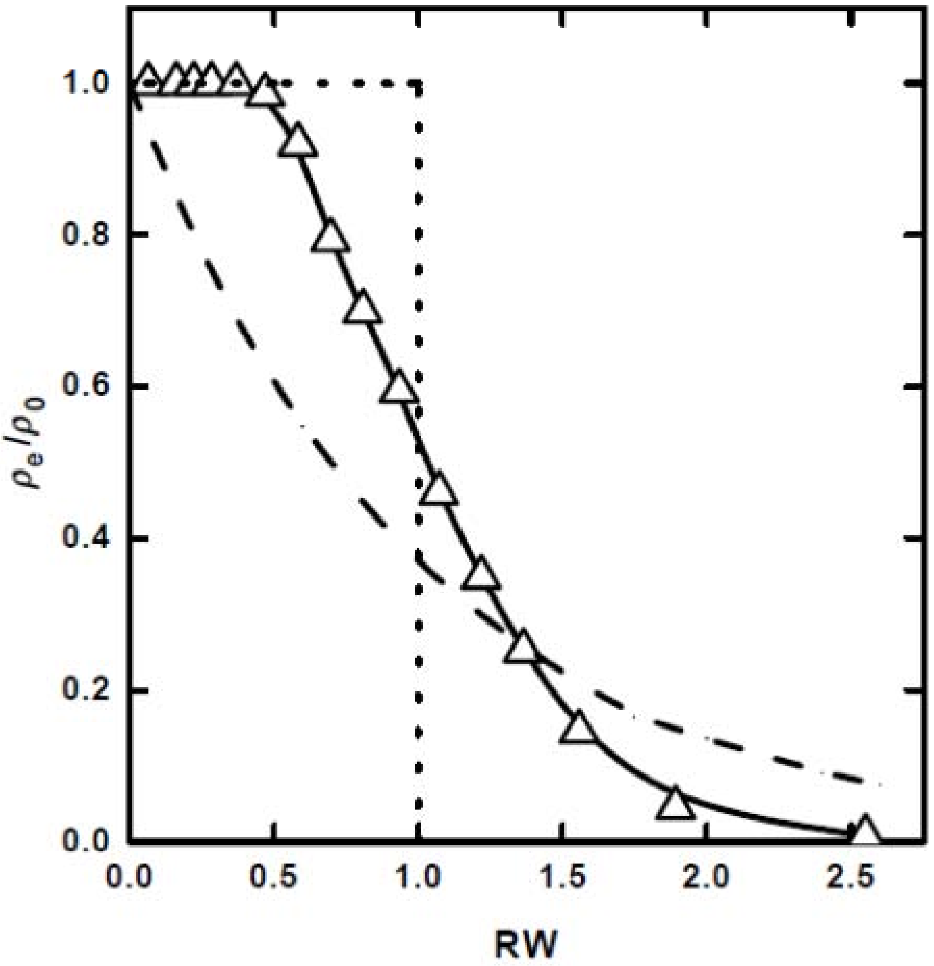

Fig.**1.** Breakthrough curve measured during washing of the spent pulping liquor **(=2.69mPa ş, =1110kgm^{-3})by the wash liquid with pH=10.9(=0.98mPa s, =998kgm^{-3})at 21°C.**Experimental data (Δ), cubic spline fit (solid line), plug flow model (dotted line), and perfectly mixed flow (dashed line).

As soon as the first portion of wash liquid passes through the bed, the concentration of lignin in the outlet stream drops rapidly. The major part of mother liquor in interparticle voids is removed and replaced by wash liquid. In the last period, only the rests of black liquor from inside narrow pores and fibre walls are removed. In contrast to the first two periods, when the liquor displacement by washing liquid is dominant, the leaching via solute desorption and diffusion from within the fibres prevails. A decrease in kappa number by approximately 4-5 units attained for pulp after displacement washing confirms the leaching of residual lignin from within the fibres (see Table 1).

b).Influence of Dispersion on the Wash Yield

The area below the breakthrough curve, expressed as the dependence of the dimensionless concentration of solute upon the wash liquor ratio, is directly proportional to the amount of alkali lignin removed from the pulp bed. Thus, the quality of the displacement washing process can be characterized by the wash yield evaluated at the wash liquor ratio equal to unity

$$\mathrm{WY}_{\mathrm{RW}=1} = \frac{\int_{RW=0}^{RW=1} \frac{\rho_e}{\rho_0} d(RW)}{\int_{RW=0}^{RW\to\infty} \frac{\rho_e}{\rho_0} d(RW)} \qquad (1)$$

Type equation here.

A measure of lignin dispersion in the bed is indicated by the dimensionless Peclet number defined as

$$\mathrm{P_e} = \frac{hu}{D\epsilon} \qquad (2)$$

This dimensionless parameter defines also the ratio of the convective to the diffusive transport mechanism. Knowing the variance of the distribution of residence time of lignin leaving a bed, the Peclet number was determined according to van der Laan [11] for a closed vessel of infinite length. Details about the Peclet number evaluation are given elsewhere [10]. Wash yield data as a function of Peclet number are illustrated in Fig. 2. In spite of various pH values of the wash liquid, it is evident that the wash yield obtained for pulp fibres is lower than that calculated according to the model derived by Brenner [12] for the packed bed of nonporous particles. In contrast to this model, when the washing process is reduced to the displacement mechanism and interfacial mixing between the displaced and displacing fluid, the leaching can play a significant role in the case of compressible porous fibres in the swollen state. The values of the wash yield are in good agreement with those obtained earlier [10, 13, 14]

Table 1. Washing Characteristics vs. pH of Wash Liquid

pH	10.9	9.5	7.7	6.2	5.0	3.8	3.25	2.5	2.15
C/%	12.3	12.2	12.3	12.4	11.9	12.1	12.0	12.7	12.3
κ	18.8	19.0	18.8	19.4	19.7	19.5	19.2	19.1	19.2
RW	6.37	6.61	6.87	6.58	6.44	7.32	5.57	8.45	7.26
m/g	2.09	2.10	2.18	2.02	2.15	2.10	2.04	2.06	2.01

C - bed consistency, κ - kappa number of pulp after washing, RW - final wash liquor ratio, m - the mass of lignin removed from
the bed by washing.

Table 2. Axial Dispersion Coefficient and Mobility Ratio Evaluated for Superficial Wash Liquid Velocities Attained at Experiments

$u.10^4/ms^{-1}$	0.50	0.67	0.75	1.00	1.12	1.43	2.04	3.28	4.68
$D.10^6/m^2 s^{-1}$	0.21	0.31	0.28	0.33	0.38	0.57	0.77	1.51	1.53
MR	0.70	0.70	0.79	0.76	0.87	0.81	0.98	0.97	1.36

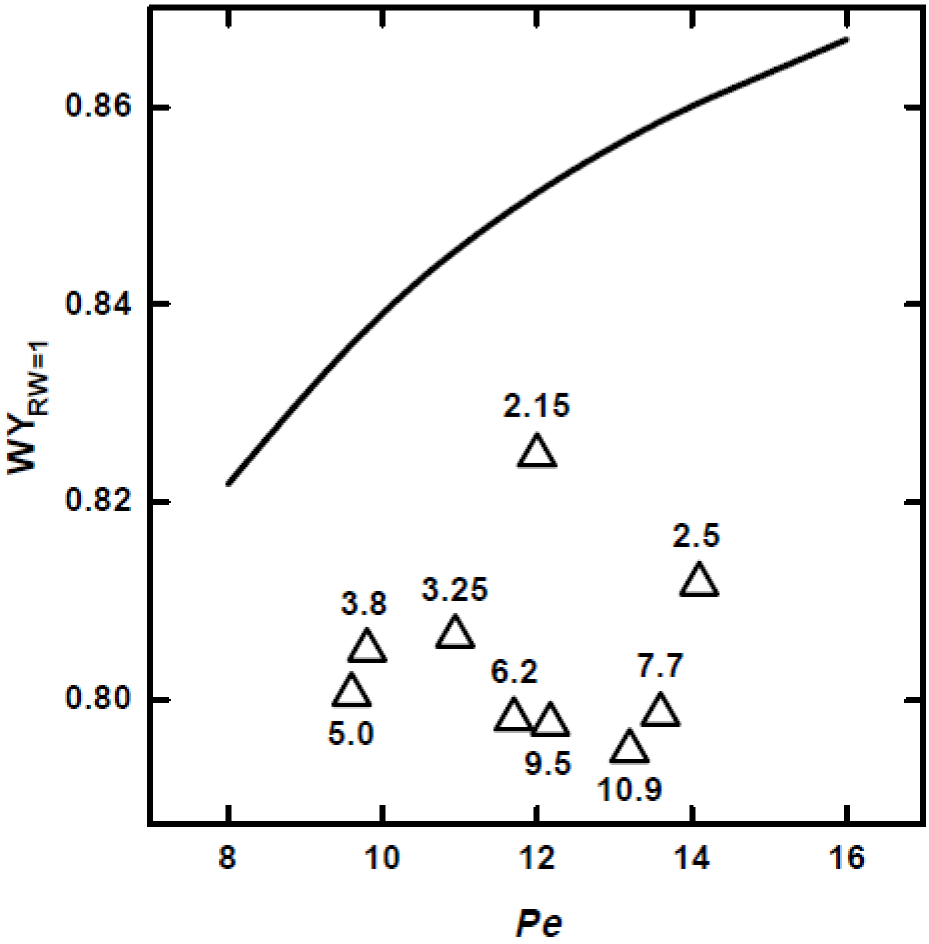

Fig. 2. Wash yield as a function of Pe for different pH values (ɵ) of wash liquid. Solid line calculated according to Brenner [12], for packed bed of nonporous particles.

Dispersion coefficient, D, from the Peclet number definition is analogous to and has the same units as diffusion coefficient. According to Sherman [15], the dispersion coefficient in beds of granular and synthetic fibrous media is of the order of 10^{-6} m^2 S^{-1} for the displacement velocities normally encountered in practice. From experimental data (Table 2), linear relationship between the dispersion coefficient, D, and the superficial wash liquid velocity, u, was obtained with a correlation coefficient of 0.97.

$$D = 3.71x10^{-3} u \qquad (3)$$

Equation (3) was derived for the superficial wash liquid velocity ranging from 5×10^{-5} m s^{-1} to 4.7×10^{-4} m s^{-1}. These results are in agreement with those obtained by Montillet et al. [16] who studied packed beds formed by spheres, Raschig rings, and nickel foams. For the superficial wash liquid velocity ranging from 3×10^{-4} to 1.3×10^{-2} m s^{-1}, Sherman [15] reported that the mixing parameter, D/u, was a constant for given bed composed of viscous or Darcon fibres and was found to be 4×10^{-4} - 1.3×10^{-3} m, depending upon physical characteristics of fibre medium. Mixing parameter, D/u, depends on the pore size distribution in a bed of packed solids. The wider the pore size distribution, the larger will be the velocity variations and the mixing parameter. Dispersion coefficient, which is a measure of the rate at which material will spread axially in the system, increases with increasing superficial velocity of the wash liquid. In porous media, dispersion is created by both the microscopic differences in velocity which exist in the interstices between fibres and large scale or macroscopic effects such as channelling. Viscosity and/or density differences can lead to unstable displacement, i:e: the formation of viscous fingers or a gravity tongue of displacing fluid in the resident liquor. These effects tend to lengthen the mixed zone between both miscible fluids. Although mother liquor and wash liquids have matched densities (see Fig. 1), viscous fingering results if the displacing fluid penetrates at unlike rates in a cross-section of the porous bed. This initial preferential penetration should be attributed to the local heterogeneities in permeability. However, Nunge and Gill [17] remind that, for less viscous, less dense displacing fluid, a critical flow rate exists below which the displacement is stable. With respect to the channelling of the displacing liquid through more viscous solute-rich liquor, the mobility of the displacing fluid (defined as the ratio of permeability to viscosity) is more significant than the straight viscosity. The mobility ratio is defined as the mobility of the displacing fluid (wash liquid) divided by the mobility of the resident fluid (mother liquor)

$$MR = (B\,\mu^{-1})_{WL} / (B\,\mu^{-1})_{ML} \qquad (4)$$

Lee [18] reported that when the mobility of the displacing fluid is lower than the mobility of the displaced liquid the tendency for channelling is suppressed. Favorable effect of lower mobility of nonionic Polyacrylamide solution in comparison with water on the displacement washing efficiency was observed also in [19]. The influence of the mobility ratio on dispersion coefficient is obvious from Table 2. In spite of the scatter in data, a trend of the dispersion coefficient increase with increasing mobility ratio is evident. It is worth mentioning that in the present experiments the mobility ratio depended on the wash liquid velocity. It follows from Table 2 that a reduction in the mobility ratio with decreasing wash liquid velocity was reached. Fluid particle dispersion found at given pressure gradient is connected with the difference of speed at which the fluid particles travel in pores with different diameters. Pulp fibre beds tested in the resent study may be characterized as compressible unmovable beds, although they differ each other by the local porosity as well as space orientation of the fibres within the bed.

c).Influence of pH on the Wash Yield

Kraft lignin recovery with lignin for sale as a byproduct has been practiced using acid precipitation [20]. In the weakly acidic region, reduced fibre swelling and improved dewatering can have a favorable effect on the washing process. Literature sources agree that maximum swelling of unbleached Kraft pulps is observed near the pH value of 9. Therefore, the influence of the wash liquid pH on the displacement washing efficiency was investigated as well. Fig. 3 shows the wash yield, $WY_{RW} = 1$, evaluated from equation (1) as a function of the wash liquid pH value. It is evident that a decrease in pH can lead to the increase of washing efficiency. Taking into account the results presented in Fig. 2, it may be assumed that the washing effectiveness depends not only upon the pH of wash liquid, but also on the dispersion of lignin in the pulp fibre bed. On the basis of experimental data, the following correlation was derived for the quantitative evaluation of the effect of dispersion and pH of wash liquid on the wash yield

$$WY = 0.80\, pH^{-0.019}\, Pe^{0.015} \qquad (5)$$

The suitability of eqn (5) was judged on the basis of the mean relative quadratic deviation of the wash yield, (defined in Symbols), which was 0.4%.

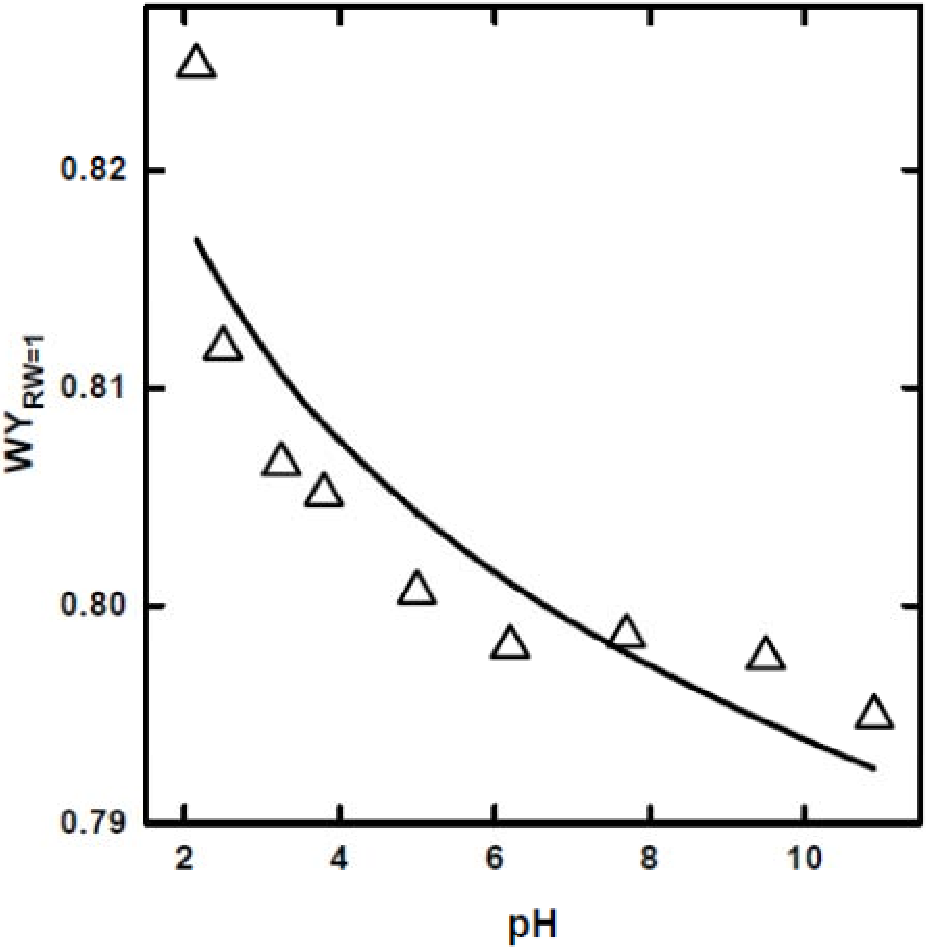

Fig. 3. Influence of pH on the wash yield. Experimental data (Δ), fit by eqn (5) for Pe = 12 (solid line).

The values of the pH and those of the Peclet number varied within the limits of 2.1-10.9 and 9.6-14.1, respectively. Since the values of regression coefficients, which were evaluated by the least-squares method, represent an estimate of the real values, the 95 % confidence intervals were also calculated. They are for the coefficient (0.77; 0.83), for the power of the pH (−0.022; −0.016), and for the power at the Peclet number (0.004; 0.026).In spite of little amount of experimental data, the correlation (5) confirmed that, in accordance with our previous papers [10, 13, 14], the wash yield depends on the Peclet number in a small degree. The solid line in Fig. 3 represents a plot of the wash yield as a function of the pH value, evaluated from eqn (5) for Pe = 12. Thus, a change in pH value from 10.9 to 2.1 resulted in an increase in the wash yield from 79.4 % to 81.8 % under given experimental conditions. In spite of the fact that the pH of wash liquid varied in the wide range, the mass of lignin removed during displacement washing was approximately the same (Table 1), at least within the error of measurement. Nevertheless, Smith et al. [21] reported that the amount of lignin removed from pulp by leaching was significant at higher pH. Many variables affect the mass transfer of the large lignin molecules out of the fibre walls during washing. The rate of leaching is limited by pore restrictions in the fibre walls, the sizes of which are controlled by the chemical environment, and the fibre swelling. Other variables that control diffusion, like the concentration-gradient driving force and the characteristics of the diffusing substance, also must be considered.

Conclusion

Displacement washing of pulp fibres is affected by a number of phenomena occurring in porous medium (pore size distribution, different local porosity of the bed, geometrical properties of fibres including their swelling, intrinsic properties of miscible fluids, sorption, electro kinetic phenomena, and others). Owing to the complexity of miscible displacement process in the pulp fibre bed, further studies should arise to explain, at least partially, many problems concerning this process.

Symbols

B: Permeability	m^2
C: Consistency of pulp bed	%
D: Axial dispersion coefficient	$m^2\ s^{-1}$
h :Thickness of bed	m
MR: Mobility ratio defined by eqn (4)	
M: Mass of lignin	g
n :Number of measurements	
Pe: Peclet number defined by eqn (2)	
RW: Wash liquor ratio	
t Time from start of experiment	s
u :Superficial wash liquid velocity	$m\ s^{-1}$
WY_{RW} =1 wash yield at RW = 1 defined by eqn (1)	

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