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New Technology of KCl Flotation Using Mixed Amine

D. Li[1], N. Xue[1], F.Q. Cheng[1,*], Z.P. Du[1] and C.Y. Sun[2]

[1]Institute of Resources and Environmental Engineering, Shanxi University, No. 92 Wucheng Road, Taiyuan 030006, Shanxi Province, P.R. China
[2]School of Chemistry and Chemical Engineering, Qinghai University, No. 251 Ningda Road, Xining 810016, Qinghai Province, P.R. China

*Corresponding author: Tel/Fax: +86 351 7016893; E-mail: cfangqin@sxu.edu.cn

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This paper studied the flotation recovery of KCl using a mixture of different carbochain amines as the collector in KCl flotation process. The results indicated that a much higher recovery of KCl was obtained through optimization of a mixed amine collector. Contact angle measurements revealed that mixed amine collectors further increased the hydrophobicity of the crystal surface of KCl. The solution surface tension could be reduced to 43 mN/m at 25 °C when the mixed amine was used. The aggregate size of mixed collector and the turbidity of the flotation solution showed that the dispersion of mixed amine colloids was better than that of octadecylamine collectors.

Keywords: Potassium Chloride, Mixed Amine, Flotation.

INTRODUCTION

As one of the three major agricultural fertilizers, over 80 % of the world's potash is produced by the selective flotation of KCl (sylvite) from NaCl (halite) and other gangue minerals. The collector is crucial in the flotation process and normally the collectors are long-chain amine which generally containing 12 to 18 carbon atoms in the aliphatic chain[1]. Among them, octadecylamine (ODA) is one of the most commonly used collectors in the market. However, the performance of octadecylamine at low temperature is not satisfying, resulting in poor flotation recovery, serious waste of collector, high production costs and poor product quality in the cold weather. Therefore, the availability of a collector applicable to the flotation of KCl would be desirable.

Development of new collectors has been focused on modifications to the molecular structure of the reagent and development of technologies involving composite reagents. Tang exploited QHS-3 anti-flotation agents using a reagent modification technique, which were then suitable for winter KCl production[2]. Titkov suggested that increased hydration of the surface of KCl crystal with rising temperature in saline solutions may reduce amine adsorption. Therefore he developed a cationic collector to improve KCl flotation recovery in the summer using technologies involving composite reagents[3]. Hancer *et al.*[4,5] studied the flotation mechanisms of dodecylamine, octadecylamine and SDS[4,5]. They indicated that hydration phenomena at salt surfaces provide a reasonable explanation for the flotation of alkali salts; implying that octadecylamine should perform better as a collector than dodecylamine or SDS. Zhou *et al.*[6] thought that a compound system containing two or more surface-active agents is better than a single surfactant system.

In this study, we introduce a mixed amine collector which can improve KCl flotation recovery even by the way of reagent composite. The mechanism of KCl flotation using mixed amine has been determined through measurement of contact angle, surface tension, turbidity, particle size and micro-flotation, *etc*.

EXPERIMENTAL

Potassium chloride (KCl) was purchased from Tianjin Damao Chemical Reagent Factory. Octadecylamine hydrochloride (ODA) and dodecylamine hydrochloride (DDA) with a purity of 99 % were obtained from Tokyo Kasei Kogyo Co., Ltd. Eicosanoic amine (C_{20}) with a purity of 80 % was purchased from Sichuan Tianyu grease chemical Co., Ltd. KCl crystals for contact angle measurements were obtained from International Crystal Laboratories. All materials were used as received without further purification. Chemical Millipore water (Milli Q, Millipore Corp., 18 MX) was used for all experiments.

Potassium chloride (KCl) saturated solution was prepared by dissolving a sufficient quantity of KCl in Millipore water while continuously stirring for 24 h at 25 °C. Saturated solutions were stored at 25 °C overnight and filtered before use.

Freshly made 10^{-2} and 10^{-3} mol/L surfactant (octadecylamine and dodecylamine) stock solutions were prepared by dissolving a calculated quantity of solid dodecylamine or octadecylamine in Millipore water while stirring at 85 °C.

Freshly made 10^{-2} and 10^{-3} mol/L eicosylamine hydrochloride stock solutions were prepared by dissolving the required mass of solid sample in the appropriate volume of water at 85 °C and then adding an appropriate amount of hydrochloride to the dissolved solutions while continuously stirring. The required amount of amine stock solution was added to KCl saturated solution to obtain the indicated concentration of test solution at 25 °C.

Contact angle measurements: Contact angles were measured using the captive-bubble technique with a JC2000C1 goniometer (Shanghai Zhongchen, Inc.)[7]. The optical system of this goniometer has independent rotational crosshairs and an internal protractor readout calibrated in 0.05° increments. For each measurement, a 50 mm × 25 mm × 6 mm KCl crystal was first dry polished with 600-grit sandpaper. After removing residual particles with compressed air, the KCl crystal was plasma treated for 5 min to obtain a fresh and smooth crystal surface and the treated KCl crystal then positioned on two stable supports in a rectangular glass chamber. The glass chamber with sample was filled with saturated KCl solution with collectors at a known concentration. The system was incubated for 8 min to allow equilibration, after which air bubbles (2-3 mm) were released using a syringe below the crystal surface. After bubble attachment, the angle of the three-phase contact line was measured at 5 min intervals on both sides of the bubble at 25 °C.

Micro-flotation tests: The micro-flotation experiments of KCl at 25 °C were carried out by using a 125 mL column cell (20 × 220 mm) with a fine filter frit (10 μm) under continuous magnetic stirring. Dried KCl (2 g, 80-100 meshes) was used each time. After 15 min stirring of the brine added with certain collector, 2 g KCl (solid particles in 80-100 meshes) was introduced into the brine and the sample stirred for a further 15 min. The samples were floated for 1 min using nitrogen at a flow rate of nitrogen at 30 mL/min. The recovered KCl was treated by vacuum-filter and washed with water-free alcohol then dried in an oven at 105 °C for 2 h. Final flotation products were cooled to 25 ºC in air and weighed. Fractional recovery was calculated as weight divided by 2 g. Micro-flotation experiments on KCl at 5 °C were accomplished in a water bath to maintain the temperature. Carefully calculated quantities of collector and KCl brine were directly added into the column cell.

Surface tension measurements: The surface tension of each brine solution was measured using the Du Noüy ring method at 25 °C (Shanghai Fangrui, Inc.). All glassware used in the experiments was washed with chromic acid and rinsed with deionized water to reduce contamination. The platinum ring (9.55 mm in diameter) was washed with acetone, methanol and deionized water respectively, followed by flame treatment to remove organic contamination. For each measurement, 30 mL samples of brine with known concentrations of octadecylamine and mixed amine were present.

Aggregate size measurement: The size of amine aggregates in KCl saturated brine was measured at 25 °C using the Eyetech Particle Size and Shaper Analyzer (Ankersmid Instruments Corporation). The effects of collector concentration on particle size of both mixed amine and octadecylamine collector were examined. Each measurement was repeated three times and the mean value was recorded.

Turbidity measurement: The turbidity of brine solutions was measured using a Laboratory turbidimeter (HACH Instruments Corporation). The concentrations of the different types of amine collectors in the KCl saturated brine were 1×10^{-5} mol/L and 5×10^{-5} mol/L. Each measurement was repeated three times and the mean value was recorded.

RESULTS AND DISCUSSION

Contact angle measurements: Contact angle, an important parameter characterizing the wetting relationship between solids and liquids, reflects the adsorption of the collector at a surface, which can be used to measure the effect of the collector on the local hydrophobicity at that surface[8-10].

The contact angle at the surface of the KCl crystals in a saturated solution containing the indicated collector mixture was plotted as a function of relaxation time (Fig. 1). The total concentration of collector mixture was held at 1×10^{-5} mol/L, in which molar ratios were octadecylamine alone, 70 % octadecylamine with 10 % dodecylamine and 20 % C_{20}, 60 % octadecylamine with 20 % dodecylamine and 20 % C_{20}, 40 % octadecylamine with 40 % dodecylamine and 20 % C_{20}, 20 % octadecylamine with 60 % dodecylamine and 20 % C_{20} and 80 % dodecylamine with 20 % C_{20}.

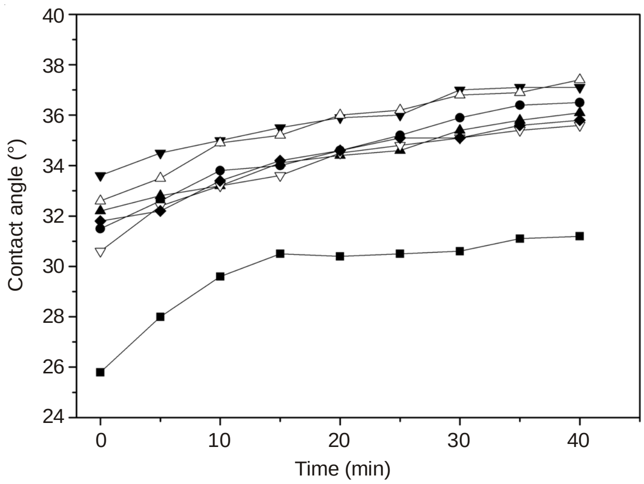

Fig. 1. Captive bubble contact angles of saturated brines at KCl crystal surface with the addition of DDA, ODA and C_{20} mixtures at different molar ratios for a total concentration of 1×10^{-5} mol/L (■: ODA alone; ●: 70 % ODA, 10 % DDA and 20 % C_{20}; ▼: 60 % ODA, 20 % DDA and 20 % C_{20}; △: 40 % ODA with 40 % DDA and 20% C_{20}; ▲: 20 % ODA with 60 % DDA and 20 % C_{20}; ▽: 80 % DDA and 20 % C_{20})

As shown in Fig. 2, the contact angles at surface of KCl crystal for all collector mixtures were much higher than the result for octadecylamine alone indicating increased hydrophobicity. In particular, for a mixed amine solution with a molar ratio of dodecylamine 20 %, octadecylamine 60 % and C_{20} 20 %, the highest contact angles were obtained. This mixture was therefore selected as a mixed amine collector for further experiments.

The influence of collector concentration on the contact angle at the KCl crystal surface was investigated at 25 ºC (Figs. 3-5). Contact angles increased with increasing collector concentration implying an increase of in collector adsorption due to higher concentration.

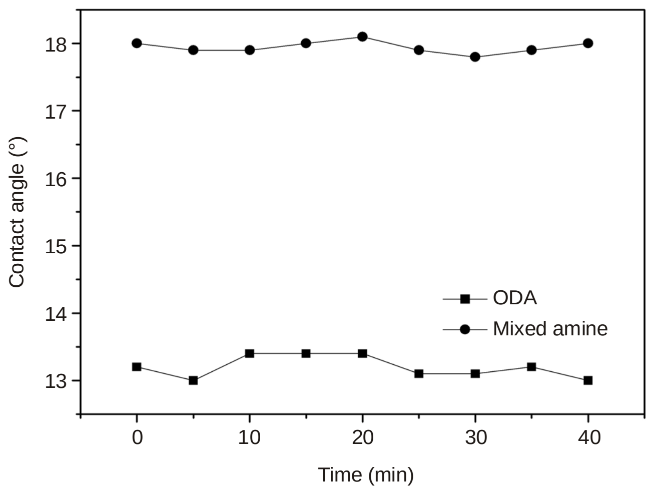

Fig. 2. Captive bubble contact angles at KCl salt surface with the addition of mixed amine and octadecylamine (ODA) collector in saturated KCl solution (Concentrations were 3 × 10^{-6} mol/L)

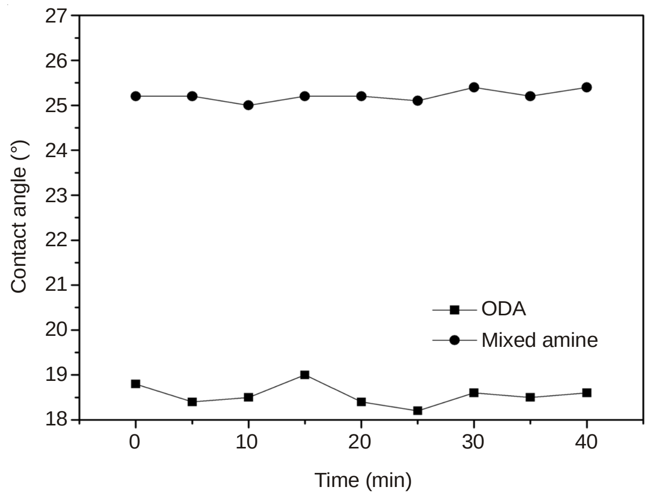

Fig. 3. Captive bubble contact angles at KCl salt surface with the addition of mixed amine and octadecylamine (ODA) collector in saturated KCl solution (Concentrations were 5 × 10^{-6} mol/L)

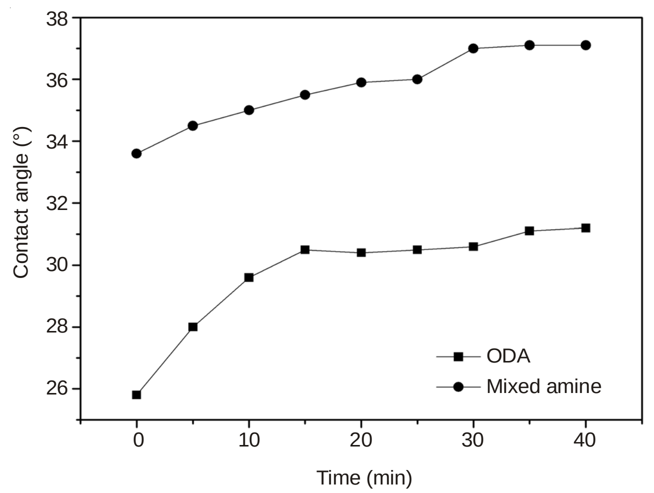

Fig. 4. Captive bubble contact angles at KCl salt surface with the addition of mixed amine and octadecylamine (ODA) collector in saturated KCl solution (Concentrations were 1 × 10^{-5} mol/L)

It is also clear that at all concentrations measured, the contact angle at the surface of the crystal was substantially

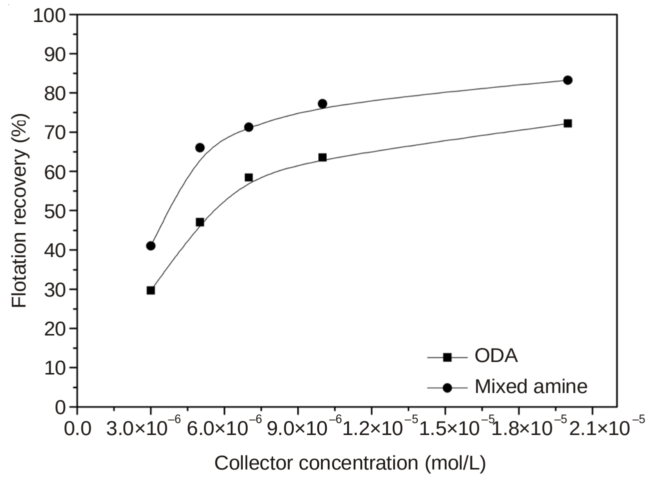

Fig. 5. Flotation recovery of KCl in the KCl saturated solution using two different collectors at 25 °C

higher in the case of a mixture of amine solutions than for octadecylamine alone, indicating a greater increase in surface hydrophobicity due to the adsorption of the mixed amine. At low collector concentrations *e.g.* 3 × 10^{-6} mol/L or 5 × 10^{-6} mol/L, the amine collectors exist primarily as independent molecules, so dodecylamine molecules may adsorb at the KCl crystal surface alongside octadecylamine and C_{20}, increasing the amount of amine adsorption and concomitantly the hydrophobicity. On the other hand, at higher concentrations *e.g.* 1 × 10^{-5} mol/L, octadecylamine precipitates form extensively, dodecylamine enhances the dispersion of amines in brine as a type of frother and amines then precipitate at the bubbles surface[11].

KCl flotation with octadecylamine and mixed amine as a collector: We recorded the flotation recovery of KCl salt from saturated solution as a function of collector concentration with both the selected amine mixture (dodecylamine 20 %, octadecylamine 60 % and C_{20} 20 %) and octadecylamine as collectors at 25 °C (Fig. 6). It was observed that the recovery of KCl salt was closely related to the concentration of the collector, but that an amine mixture improved the recovery of KCl by approximately 15 % at all concentrations measured. This result suggested a synergistic effect produced by amine mixture collectors, which improved KCl recovery from saturated brine.

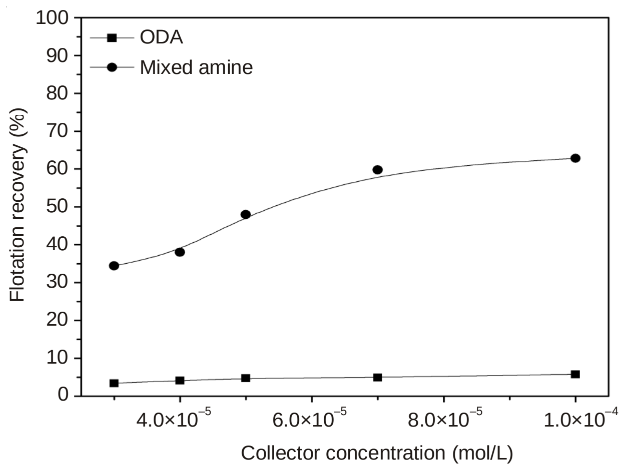

Fig. 6. Flotation recovery of KCl in a saturated solution using two different collectors at 5 °C

Fig. 6 shows the change of KCl recovery with collector concentration at 5 °C. It can be seen that less than 10 % of KCl was floated when octadecylamine alone was used as a collector. However, at 5 °C the collecting activity of the selected amine mixture was significantly higher and over 60 % of KCl salt was recovered at a collector concentration of 7×10^{-5} mol/L. The poor flotation recovery of KCl using octadecylamine alone suggested that serious colloid aggregation occurred, reducing adsorption of octadecylamine. Therefore, there may be a synergistic effect between dodecylamine, octadecylamine and C_{20}, improving the floatation recovery due to an increase in adsorption at the surface of KCl crystals, especially at low temperature.

Surface tension measurements: It is well known that the adsorption property of the collectors at the surface of KCl crystals in a saturated solution is closely related to the concentration of the collector, which plays an important role in the flotation behavior of KCl particles. Static surface tension was measured to evaluate surface adsorption of mixed collectors. Surface tension was plotted against collector concentration in saturated KCl solution (Fig. 7). The saturated adsorption concentrations (SACs) of collectors were obtained by determining the intersection point of the plateau portion and the steeply downward sloping portion of these plots. The surface tension at SAC (γ_{SAC}) was calculated by analysing the plateau region of the plots. Values of SAC and γ_{SAC} were 6×10^{-6} mol/L and 43.4 mN/m, 1×10^{-5} mol/L and 60.8 mN/m for the selected mixed amine and octadecylamine, respectively.

According to Gibbs' law, at equilibrium, adsorption of collectors at a surface leads to a reduction of the surface tension. The maximum interfacial excess concentration in moles per square metre, Γ_{max} and the minimum area per molecule, A_{min}, per collector molecule can be calculated using the Gibbs adsorption isotherm equations (eqns. 1 and 2)[12].

$$\Gamma_{max} = \frac{1}{2.303RT}\left(-\frac{\partial \sigma}{\partial \log c}\right)_T \quad (1)$$

$$A_{min} = 10^{20} / (N\Gamma) \quad (2)$$

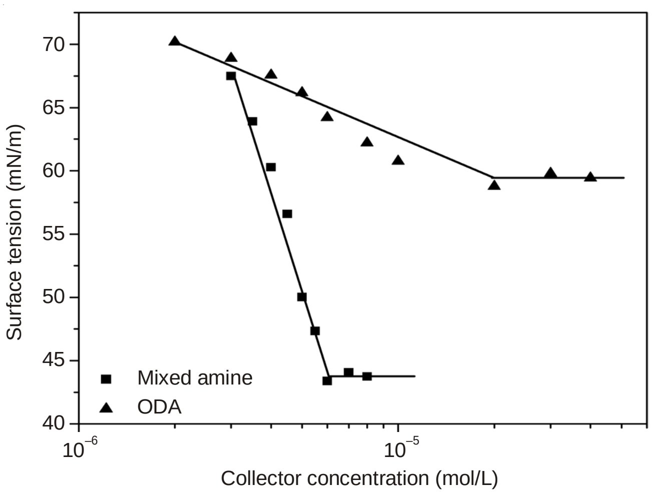

Fig. 7. Surface tension of saturated KCl solution as a function of octadecylamine (ODA) or mixed amine concentration

where $\partial\sigma/\partial \log c$ is the slope of the surface tension (Table-1). Γ_{max} and A_{min} both reflect the arrangement of collector molecules at the interface. Octadecylamine has a much smaller Γ_{max} value than mixed amines, which is consistent with the larger γ_{sac}, as discussed above due to the loose molecular arrangement at the interface. Correspondingly, octadecylamine has a larger calculated A_{min}, which varies inversely with Γ_{max}. It appears that octadecylamine adsorption at an interface provides insufficient hydrophobicity for KCl flotation. However, the low A_{min} value recorded for our amine mixture indicates much more collector molecular adsorption at the surface and so it can provide enough hydrophobicity for KCl flotation. Thus the flotation recovery of KCl is higher.

TABLE-1
VALUES OF THE Γ AND A FOR OCTADECYLAMINE AND MIXED AMINE

Collector	Γ (mol m^{-2})	A (n m^{-2})
Octadecylamine	2.2×10^{-6}	0.83
Mixed amine	14.5×10^{-6}	0.11

Aggregate size and turbidity measurement: For a water insoluble amine collector, a smaller colloid size will give a higher efficiency of adsorption at the solid surface. In order to evaluate the effect of colloid size and given that amine collectors form amorphous precipitates, the colloid size distribution was determined at different collector concentrations (Fig. 8). It is interesting to note that the mixed amine colloid is smaller than pure octadecylamine colloid. This result indicates that the dispersion of mixed amine collectors is better than that of octadecylamine. This change would be beneficial for the flotation of KCl particles and is in accordance with the results of micro-flotation experiments.

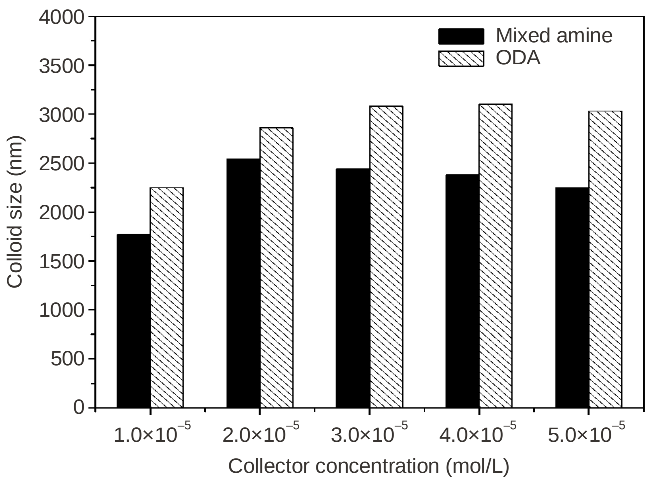

Fig. 8. Colloidal size distribution for mixed amine and octadecylamine (ODA) collectors in saturated KCl solutions

The turbidity of saturated KCl solutions was measured to further investigate the function of the mixed amine collector. The results are listed in Table-2. The turbidity is reduced at collector concentrations of 1×10^{-5} and 5×10^{-5} mol/L for mixed amines. This suggests that the solubility of mixed amines is greater than that of octadecylamine, which could improve the flotation recovery of KCl particles.

TABLE-2
TURBIDITY OF SATURATED KCl SOLUTIONS ON THE ADDITION OF DIFFERENT AMINE COLLECTORS

Collector concentrations (mol/L)	Turbidity (NTU)	
	Octadecylamine	Mixed amine
1×10^{-5}	4.547	3.417
5×10^{-5}	23.317	17.487

Conclusion

In this study the flotation recovery of KCl particle using mixing amine as the collector. The results indicated that a much higher flotation recovery can be obtained using mixed amine collectors. The contact angles at KCl crystal surfaces in saturated KCl solutions with different collectors (octadecylamine and mixed amine) were measured using the captive-bubble technique. The presence of mixed amine collectors produces greater hydrophobicity at the KCl crystal surface than octadecylamine alone. The surface tension of solution is lower when the collector is mixed amine for the same collector concentration. Colloid size distribution results indicated that the dispersion of mixed amine colloids is better than the octadecylamine collectors. Due to these reasons the flotation recovery of KCl is higher when the collector is mixed amine.

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