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# Mixed convection in the copper dissolution technique of studying mass transfer

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## Abstract

The rate of mass transfer between the wall of a tube and a liquid flowing laminarily through the tube has been studied with the copper dissolution technique. The experiments revealed a significantly higher rate of mass transfer than predicted by the theoretical solution of the Graetz–Nusselt problem. The cause for this deviation was traced to natural convection induced by an increase in liquid density near the wall of the tube. An improvement to the copper dissolution technique is suggested that is shown largely to eliminate natural convection.

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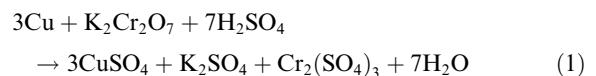
*Keywords:* Mass transfer measurement; Copper dissolution; Natural convection; Mixed convection; Graetz–Nusselt problem

## 1. Introduction

The experimental study of mass transfer processes routinely faces the obstacle of deducing the rate of individual transport steps from measurements in which the effect of several steps are lumped together. A host of experimental techniques have been developed to solve this problem and have been reviewed e.g. by Poulson and Robinson [1]. The most common and straightforward approach is to devise an experiment in which the transport resistances of all interfering effects are so low that their influence on the experimental observation becomes negligible compared with the principle mass transfer step being studied.

One such technique for the measurement of the liquid transport coefficient in mass transfer between a liquid and a solid surface is the copper dissolution method proposed by Gregory and Riddiford [2]. It involves contacting a solution of 1 mol/l sulphuric acid containing 30 mmol/l potassium dichromate with a copper surface. The dichromate anion acts as an oxidation

agent and oxidises the copper according to the following overall equation:



where chromium is reduced from  $\text{Cr}^{(\text{VI})}$  to  $\text{Cr}^{(\text{III})}$ . Gregory and Riddiford showed the reaction rate to depend solely on the rate of mass transfer to the wall and the log-mean mass transfer coefficient can be computed directly from the decline in  $\text{Cr}^{(\text{VI})}$  concentration:

$$k_L = \frac{\dot{V}}{A_w} \ln \left( \frac{C_x}{C_w} \right) \quad (2)$$

In the four decades since the original publication, considerable experience in using this method has been documented in the literature and the key-parameters of the system, such as the diffusion coefficient of the dichromate ion appear well established [3–6]. We therefore chose this method for the experimental study of mass transfer in a two-phase regime of pipe flow known as bubble-train flow [7].

Before embarking on the experimental study of bubble-train flow, we undertook a series of single-phase experiments with the aim of verifying the experimental and analytical procedure. This regime of transport

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### Nomenclature

$A_w$	surface area of the inner wall of the capillary, $m^2$	$Sh$	Sherwood-number, $Sh = k_L d_i D^{-1}$
$a$	thermal diffusivity, $m^2/s$	$\bar{u}$	volume-average liquid velocity, $m/s$
$C$	molar concentration, $kmol/m^3$	$\dot{V}$	volume flow rate, $m^3/s$
$D$	Fickian diffusion coefficient, $m^2/s$	<i>Greek symbols</i>	
$d_i$	tube diameter, $m$	$\eta$	dynamic viscosity, $Pa\ s$
$g$	gravitational acceleration, $m/s^2$	$\nu$	kinematic viscosity, $m^2/s$
$Gr$	Grashof-number, $Gr = g d_i^3 \nu^{-2} (\rho_b - \rho_w) \rho_b^{-1}$	$\rho$	density, $kg/m^3$
$Gz$	Graetz-number, $d_i^2 \bar{u} D^{-1} l^{-1}$	<i>Subscripts</i>	
$k_L$	mass transfer coefficient between liquid and wall, $m/s$	b	bulk average value
$l$	tube length, $m$	bubble	in/of a gas bubble
$Pr$	Prandtl-number, $Pr = \nu a^{-1}$	lm	logarithmic mean value
$Ra$	Rayleigh-number, $Ra = Gr Pr$	w	value at the tube wall
$Re$	Reynolds-number, $Re = d_i \bar{u} \nu^{-1}$	$\alpha$	value at entrance to the capillary
$Sc$	Schmidt-number, $Sc = \nu D^{-1}$	$\omega$	value at exit from capillary

between the wall of a tube and a fluid flowing laminarily through the tube is the subject of the classic analysis developed independently by Graetz and Nusselt, who have given this problem its name. It is well suited to verifying experimental and analytical methods, because it is theoretically well understood and very precise correlations for the Sherwood-number exist. For example, Baehr and Stephan [8, p. 363], express the log-mean Sherwood-number as:

$$Sh_{lm} = \frac{3.657}{\tanh(2.264 Gz^{-1/3} + 1.7 Gz^{-2/3})} + 0.0499 Gz \times \tanh(Gz^{-1}) \quad (3)$$

where  $Gz$  is the Graetz-number defined by

$$Gz = Re Sc \frac{d_i}{l} = \frac{d_i^2 \bar{u}}{Dl} \quad (4)$$

This solution is valid for the entire range of  $Gz$  and deviates from the exact series-solution by no more than 1%.

To our surprise, though, the experimental results deviated significantly from theory. The experiments consistently showed a lower exit concentration of  $Cr^{(VI)}$  than predicted by Eq. (3). None of the previous investigations using the copper dissolution technique have reported such deviation. We thereupon subjected the copper dissolution method to a detailed analysis and remeasured many of the chemical and physical properties of the system that are essential to measuring mass transfer. In this paper, we summarise our findings and suggest an alteration to the original copper dissolution method, that will improve its accuracy.

## 2. Experimental study

### 2.1. Materials and methods

As suggested by Gregory and Riddiford [2], the feed solution consisted of 30 mmol/l potassium dichromate (CAS-No.: 7778-50-9) in 1 M sulphuric acid. It was prepared using reagent grade compounds supplied by Merck KGaA, Germany, and degassed and deionised tap water.

Copper tubing with an inner diameter of 1 and 2 mm was bought locally. The material was certified to comply with DIN 1787 SF-Cu, implying 99.90% pure copper. The tubing was cut to lengths of 270 mm. In order to obtain a chemically uniform surface, the tubes were prepared for use by rinsing their lumen with a sequence of acetone, water, potassium dichromate solution and water. Each rinse lasted for 5 min during which a flow rate of approximately 40 ml/min was maintained. After the final rinse, the tubes were blown dry.

The following equipment was used (Fig. 1). The feed solution was pumped from a 2 l glass flask with the aid of a peristaltic pump (Reglo-Analog MS-2/8-160, Ismatec, Zürich, Switzerland) using either Tygon or

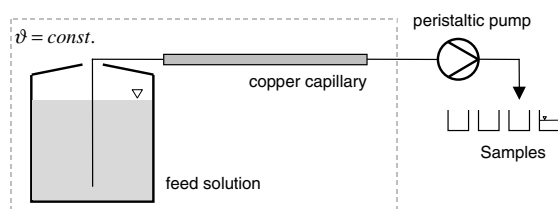


Fig. 1. Schematic representation of the experimental setup.

Viton tubing supplied by the pump manufacturer. The liquid flow rate was determined volumetrically. All tubes were interconnected with PEEK couplings. The feed flask and the copper tube were placed in a thermostatic basin which was maintained at 25 °C.

Blank test runs without a copper tube proved that there was no measurable sink for Cr<sup>(VI)</sup> in the system other than the copper. Furthermore, samples of dichromate solution were left open to the air for 6 h without a measurable decline in Cr<sup>(VI)</sup> concentration, proving that no special precautions were required for sample handling.

Sampling began 10 min after starting the flow through the capillary and three samples of 2.5 ml each were drawn at 2 min intervals for every run. Several runs were performed in one batch. The copper tubes were replaced after 8 h of operation and no significant change in inner diameter was detected.

### 2.1.1. Analytical procedure

All samples were analysed spectrophotometrically with a Varian Cary 219 spectrophotometer. Owing to the strong absorbance of Cr<sup>(VI)</sup>, the samples had to be diluted 100-fold with 1 M sulphuric acid.

Fig. 2 shows the absorption spectrum of the diluted potassium dichromate solution. In order to rule-out an interference of other species in the spectrophotometric measurement of Cr<sup>(VI)</sup>, the absorption spectra of Cr<sup>(III)</sup> and Cu<sup>(II)</sup> were measured, using solutions of 0.6 mmol/l chromium chloride and 0.9 mmol/l copper sulphate in 1 M sulphuric acid. It can be seen (Fig. 2) that the absorption around 350 nm depends solely on Cr<sup>(VI)</sup>. Furthermore, the spectrum displays a plateau at this

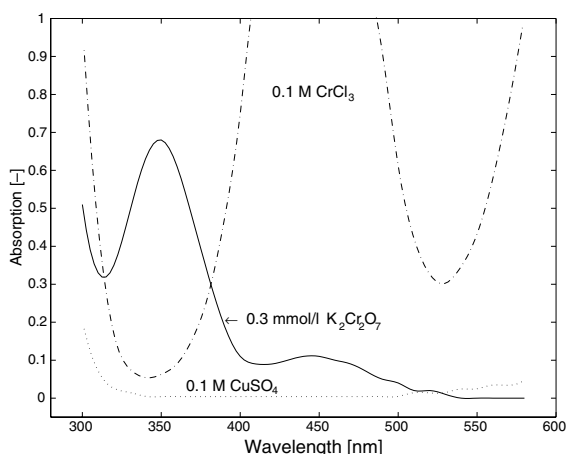


Fig. 2. Absorption spectra of 0.3 mmol/l K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 0.1 M CuSO<sub>4</sub> and 0.1 M CrCl<sub>3</sub> in 1 M H<sub>2</sub>SO<sub>4</sub>. The absorption-peak at 350 nm is suitable for measuring the Cr<sup>(VI)</sup> concentration. Note that the concentrations of Cr<sup>(III)</sup> and Cu<sup>(II)</sup> are 300 times higher than will occur in the actual samples.

wavelength, which makes the measurements insensitive to wavelength-drift.

In summary, the analytical procedure was as follows. Prior to and after each batch of measurements, a calibration curve was prepared with samples of 0.1, 0.2 and 0.3 mmol/l potassium dichromate in 1 M sulphuric acid.<sup>1</sup> From each experimental sample, two sub-samples were drawn and each was individually diluted 1:99 with 1 M sulphuric acid. Both diluted samples were measured individually. If the measured Cr<sup>(VI)</sup> concentrations differed between the sub-samples by more than 1%, the dilution was considered to be inaccurate and two new sub-samples were analysed. Otherwise the arithmetic mean of both measurements was taken to be the correct Cr<sup>(VI)</sup> concentration.

## 3. Results and discussion

### 3.1. Initial experimental results

A set of experiments was run in the range of  $Gz = 5, \dots, 450$ . The data were obtained in three independent experimental runs and each data point was measured repeatedly.

The results are shown in Fig. 3 as relative exit concentrations over  $Gz$ . The solid line is the theoretical result using Stephan's equation (Eq. (3)). The data are plotted twice: once with the diffusion coefficient for dichromate reported by Gregory and Riddiford ( $D = 0.907 \times 10^{-9}$  m<sup>2</sup>/s) and a second time with  $D$  fitted to the Stephan solution ( $D = 2.493 \times 10^{-9}$  m<sup>2</sup>/s).<sup>2</sup>

The correlation between theory and experiment is disappointing. The experiments display a significantly lower exit concentration and thus more vigorous mass transfer than theory predicts. The spread of the data is far smaller than the deviation from the theoretical result, and the error is therefore obviously systematic.

### 3.2. Causes of error in the copper dissolution method

The possible causes for the observed discrepancy are as follows:

- a flaw in the analytical procedure,
- an error in the diffusion coefficient reported in the literature,
- a shift in chemical composition near the wall resulting in more mobile Cr<sup>(VI)</sup> species,

<sup>1</sup> In all cases, both calibration curves were identical, proving the stable operation of the spectrophotometer.

<sup>2</sup> It is a peculiarity of the presentation in terms of the Graetz-number that the  $Gz$ -scale and not the concentration scale changes with  $D$ .

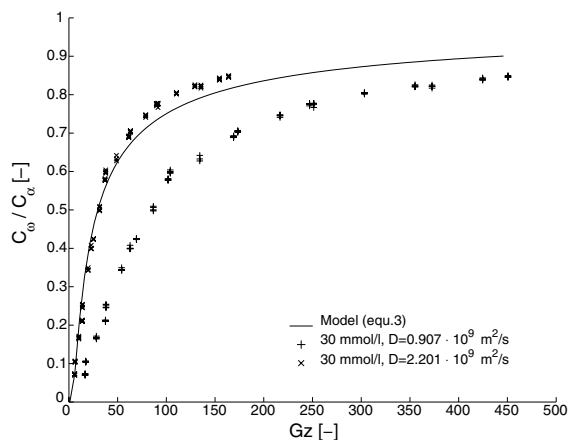


Fig. 3. Comparison of initial single-phase results with the theoretical solution according to Stephan [8, p. 363]. Experiments were performed with 30 mmol/l potassium dichromate. Data are plotted for the literature value of  $D = 0.907 \times 10^{-9} \text{ m}^2/\text{s}$  and for the least-squares fitted value of  $D = 2.201 \times 10^{-9} \text{ m}^2/\text{s}$ .

- a distortion of the flow owing to a change in viscosity at the wall,
- natural convection near the wall caused by a density increase owing to copper dissolution,
- the enhancement of Fickian diffusion by ionic drag-effects.

We shall discuss each hypothesis in turn.

### 3.2.1. The analytical procedure

This method outlined in Section 2.1.1 is well supported by the literature. In studying a very similar system,<sup>3</sup> Goeringer et al. [9] confirmed that absorption by  $\text{Cr}^{(\text{VI})}$  is strongest at  $\sim 350 \text{ nm}$  and is not interfered with by other species. The same authors cite further evidence for the choice of absorption wavelength (Refs. [1–3] in [9]). Furthermore, Lee and Stewart [10] studied the oxidation of alcohols by potassium dichromate in mineral acid solutions, including sulphuric acid. They monitored the consumption of  $\text{Cr}^{(\text{VI})}$  spectrophotometrically at 349 nm.

Given the pivotal importance of using a reliable analytical method, it was subjected to a further test. Reference samples were prepared by dissolving carefully weighed amounts of copper powder (GR grade, Merck KGaA, Germany) in 100 ml flasks of fresh feed solution (30 mmol/l potassium dichromate), thus reducing the  $\text{Cr}^{(\text{VI})}$  concentration by a defined amount. Comparison of the absorption data of these samples with copper-free

<sup>3</sup> Goeringer et al. studied the dissolution of copper by 1 mmol/l  $\text{K}_2\text{Cr}_2\text{O}_7$  in 0.2 mol/l  $\text{H}_2\text{SO}_4$ .

reference samples confirmed the predicted  $\text{Cr}^{(\text{VI})}$  concentration with negligible error. Thus the reliability of the analytical method was established beyond reasonable doubt.

### 3.2.2. The diffusion coefficient

The diffusion coefficient enters the theoretical solution via the Graetz-number (Eq. (4)). Gregory and Riddiford [2] measured the diffusivity by the sintered-pad technique and found  $D = 0.907 \times 10^{-9} \text{ m}^2/\text{s}$ . Fitting the experimental data to the theoretical curve resulted in a diffusion coefficient of  $D = 2.493 \times 10^{-9} \text{ m}^2/\text{s}$ . Not only is such an error in the original measurement of  $D$  unlikely, but the resulting alignment of theory and experiment also remains unsatisfactory (Fig. 3). With the fitted diffusion coefficient, theory underpredicts mass transfer for low and overpredicts it for higher Graetz-numbers. Thus, only a dependence of effective diffusivity on the Graetz-number could improve the fit.

### 3.2.3. Chemical composition

Such a dependence could possibly be caused by a shift in chemical composition of the system during the consumption of  $\text{Cr}^{(\text{VI})}$ . If this resulted in an increase in more mobile species, the observed effect could be explained. Discussion of this hypothesis requires a more detailed analysis of the underlying chemistry of the copper dissolution method, which has to our knowledge not been documented before.

The dichromate system—to give the solution proposed by Gregory and Riddiford a name—initially has three components: potassium dichromate, sulphuric acid and water. Potassium dichromate is the potassium salt of dichromic acid and so, given the amphoteric nature of water, we are essentially dealing with a mixture of three acids. In aqueous solution, the acids are subject to dissociation reactions which very rapidly reach an equilibrium and are linked to each other by the proton concentration in the system. Dichromic acid and sulphuric acid are bivalent acids and thus dissociate in two steps. Furthermore, the dichromate ion itself dissociates into monochromate, which in turn can reassociate in two steps to form the bivalent monochromic acid. Thus, in summary, the dichromate system comprises no less than 13 chemical species of which 9 are ionic, balanced with each other in 9 interlocking equilibrium reactions (Fig. 4).

Quite clearly, the proton concentration has a major influence on the equilibrium composition of the dichromate system. Since seven protons are consumed in the reduction of every  $\text{Cr}^{(\text{VI})}$ -ion, a marked shift in proton concentration and therefore a shift of the overall chemical equilibrium can be expected to occur near the copper surface.

In order to study such changes in composition, the system of equilibrium reactions has to be evaluated. This

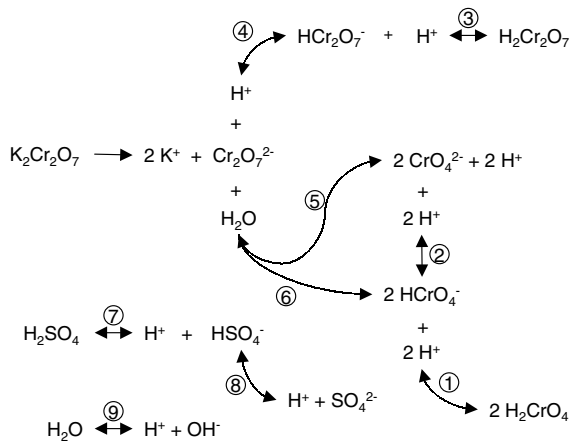


Fig. 4. Reaction pathways of potassium dichromate in aqueous sulphuric acid.

requires the knowledge of the governing equilibrium coefficients, which can be found in the literature. Table 1 gives a synopsis of the data found there. Some uncertainty arises from the fact that not all the equilibrium constants were determined for the combination of dichromate and sulphuric acid. Lee and Stewart [10] report a dependence of  $K_1$  on the proton source, which is likely to be the cause of the range of values found for this constant in the literature. No such issues are reported for the other equilibrium constants. With due caution, the following analysis should be viewed as at least qualitatively correct.

Using the equilibrium constants highlighted in Table 1 and a specially developed pseudo-time marching algorithm to solve the underlying system of non-linear equations, the composition of the dichromate system during the consumption of  $\text{Cr}^{(\text{VI})}$  was calculated (Figs. 5A and 6A).

The results show that in the fresh dichromate solution, 2/3 of the  $\text{Cr}^{(\text{VI})}$  inventory are stored in dichromates and 1/3 in monochromates. This equilibrium shifts in the course of  $\text{Cr}^{(\text{VI})}$  consumption in favour of the monochromates, which are the only  $\text{Cr}^{(\text{VI})}$  species left at the limit of complete turnover.

Making this shift in composition responsible for the increased mass transfer at higher  $\text{Cr}^{(\text{VI})}$  depletion implies that the monochromates have a significantly higher diffusion coefficient than the dichromates.

A review of diffusion coefficients found in the literature, which is summarised in Table 2, does not support this view. Vacek and Rod [14] and Iadicicco et al. [15] studied the diffusion coefficients of potassium chromate and dichromate in water. Although their results cannot be applied to the present case for lack of a background electrolyte, they support the notion that dichromates are more mobile than monochromates. Vacek and Rod suggest that this is due to the substantially lower degree of hydration of the dichromate ion which can be deduced from its lower heat of solution. Therefore the effective molecular radius of the dichromate ion is smaller than that of the monochromate, which results in a higher diffusion coefficient. The bottom line is that the dichromates appear to be more mobile than the monochromates, which contradicts the above hypothesis.

### 3.2.4. Viscosity

The next hypothesis postulates a distortion of the velocity profile caused by a change in viscosity at the wall, resulting in increased mass transfer. The dissolution of copper at the wall does in fact increase the viscosity. A measurement of the dynamic viscosity of samples of the dichromate system to which increasing amounts of copper were added shows an increase by 10% from fresh dichromate solution to complete  $\text{Cr}^{(\text{VI})}$  turnover (Fig. 7).

Table 1  
Equilibrium coefficients of chromic acid

	Chemical reaction		Source			
	Left side	Right side	[11]	[12]	[13]	
1	$\text{H}_2\text{CrO}_4$	$\xrightleftharpoons{K_1} \text{H}^+ + \text{HCrO}_4^-$	$K_1 =$	1.21	<b>0.182</b>	0.178
2	$\text{HCrO}_4^-$	$\xrightleftharpoons{K_2} \text{H}^+ + \text{CrO}_4^{2-}$	$K_2 =$	$3.7 \times 10^{-7}$	$3.24 \times 10^{-7}$	<b><math>3.55 \times 10^{-7}</math></b>
3	$\text{H}_2\text{Cr}_2\text{O}_7$	$\xrightleftharpoons{K_3} \text{H}^+ + \text{HCr}_2\text{O}_7^-$	$K_3 =$	<b>1</b>	–	–
4	$\text{HCr}_2\text{O}_7^-$	$\xrightleftharpoons{K_4} \text{H}^+ + \text{Cr}_2\text{O}_7^{2-}$	$K_4 =$	<b>0.85</b>	–	–
5	$\text{Cr}_2\text{O}_7^{2-} (+\text{H}_2\text{O})$	$\xrightleftharpoons{K_5} 2\text{H}^+ + 2\text{Cr}_2\text{O}_4^{2-}$	$K_5 =$	<b><math>3 \times 10^{-15}</math></b>	–	$2.57 \times 10^{-15}$
6	$\text{Cr}_2\text{O}_7^{2-} (+\text{H}_2\text{O})$	$\xrightleftharpoons{K_6} 2\text{HCrO}_4^-$	$K_6 =$	<b><math>2.3 \times 10^{-2}</math></b>	–	$2.09 \times 10^{-2}$

The indices refer to Fig. 4. The constants are defined in the customary way, e.g.,  $K_1 = ([\text{H}^+][\text{HCrO}_4^-])/[\text{H}_2\text{CrO}_4]$ . Water is omitted from the equation.

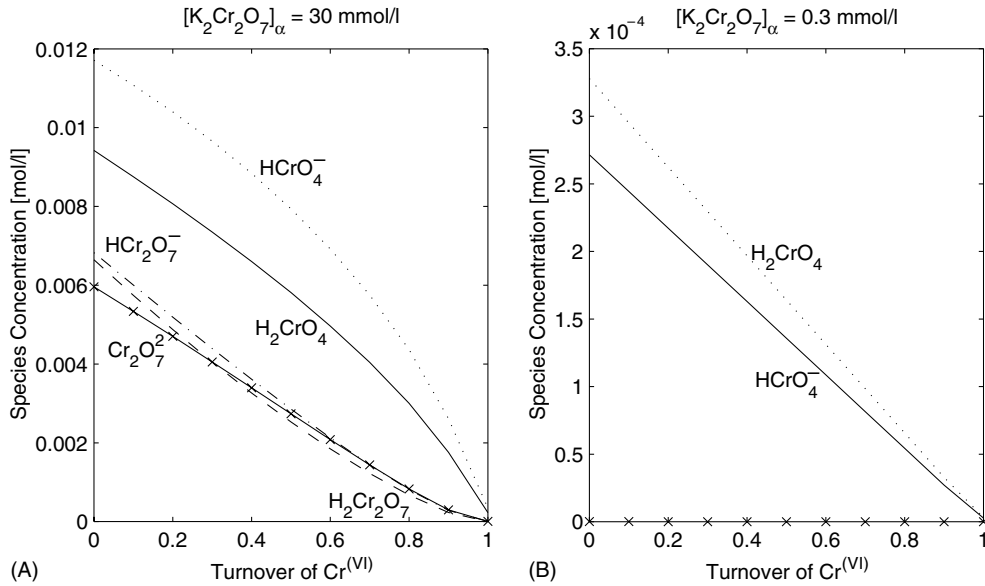


Fig. 5. Evolution of chemical composition over chromate turnover. (A) For an initial concentration of 30 mmol/l potassium dichromate (left) and (B) for an initial concentration of 0.3 mmol/l (right).

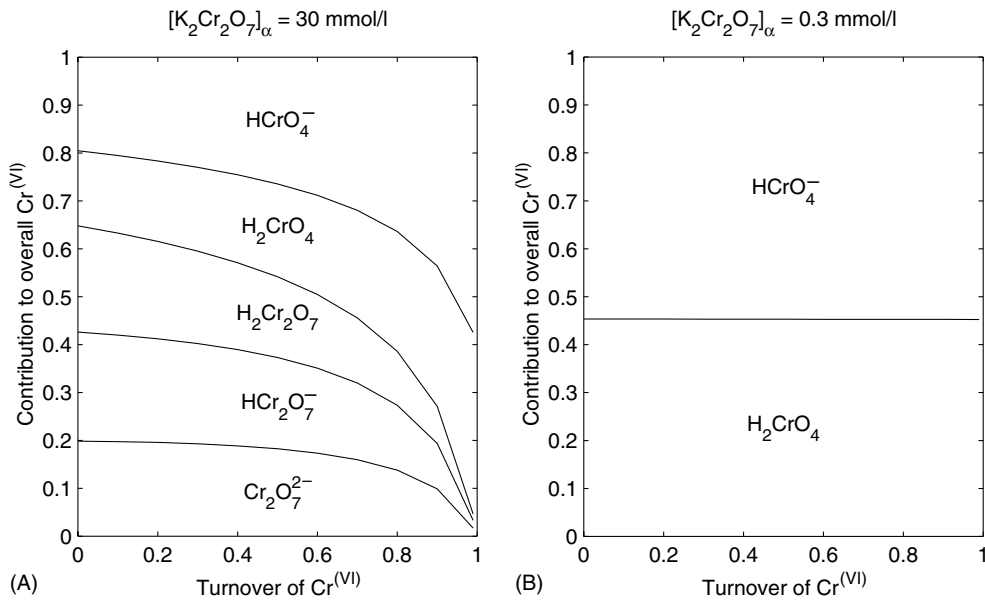


Fig. 6. Composition of the Cr(VI) inventory of the solution over Cr(VI) consumption. The amount of Cr(VI) locked-up in each species is proportional to the vertical distance between neighbouring curves. (A) For an initial concentration of 30 mmol/l potassium dichromate (left) and (B) for an initial concentration of 0.3 mmol/l (right).

An increase in viscosity at the wall would, however, impede rather than enhance mass transfer, owing to reduced diffusion coefficients and reduced convection. This fact is well established and is correlated by the Sieder and Tate-correction of the Sherwood-number:

$$Sh = \left( \frac{\eta_0}{\eta_w} \right)^{0.14} Sh_{iso} \quad (5)$$

where  $Sh_{iso}$  is the Sherwood-number of an isoviscous flow.<sup>4</sup>

<sup>4</sup> The correction factor was developed for heat-transfer problems. Note that the correction factor is larger than unity for heated walls and smaller than unity for cooled walls. The present case of mass transfer thus corresponds to cooled walls.

Table 2  
Synopsis of effective diffusion coefficients for the dichromate system found in the literature (all measurements at 25 °C)

Composition	Method	Value (m <sup>2</sup> /s)	Source
30 mM K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in 1 M H <sub>2</sub> SO <sub>4</sub>	Sintered-pad cell	9.07 × 10 <sup>-10</sup>	[2]
30 mM K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in 0.25 M H <sub>2</sub> SO <sub>4</sub>	Sintered-pad cell	1.16 × 10 <sup>-9</sup>	[2]
Inf. dilute K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in water	Taylor dispersion	1.8 × 10 <sup>-9</sup>	[14]
Inf. dilute K <sub>2</sub> CrO <sub>4</sub> in water	Taylor dispersion	1.5 × 10 <sup>-9</sup>	[14]
Inf. dilute K <sub>2</sub> CrO <sub>4</sub> in water	Gouy diffusimeter	1.45 × 10 <sup>-9</sup>	[15]

### 3.2.5. Density

The dissolution of copper at the wall causes a change not only in viscosity but also in density. The change is not substantial: density measurements of the same samples that were used to measure the viscosity show a difference of merely 0.91% between fresh dichromate solution and exhausted solution containing the corresponding amount of copper.<sup>5</sup> It will be shown, however, that this density gradient is quite sufficient to induce natural convection in the capillary. In a horizontal capillary, the dense outer liquid layer flows down in circumferential direction, thus inducing tangential and radial motion in the hitherto purely translational flow. This natural convection results in increased mass transfer to the wall.

This new regime of forced and natural convection is known as mixed convection and its implications on heat-transfer have been studied extensively. Solutions for horizontal tubes have been reviewed by Shome and Jensen [16] and those for vertical tubes are reviewed by Zeldin and Schmidt [17].

The degree of natural convection is generally described in terms of the Grashof- and Prandtl-numbers or their combination, the Rayleigh-number:

$$Gr = \frac{g d_i^3}{\nu^2} \left( 1 - \frac{\rho_b}{\rho_w} \right) \quad (6)$$

<sup>5</sup> This would be the density at the wall only if the copper ions diffuse at the same speed as the Cr<sup>(VI)</sup> species. Slower copper diffusion would lead to a higher density change while faster diffusion would result in a lower increase in density. In all cases the bottom line is the same, so it is sufficient for the present purposes to assume a density increase of approximately 1% at the wall.

$$Pr = \frac{\nu}{a} \quad (7)$$

$$Ra = Gr Pr \quad (8)$$

The usual analogy between heat and mass transfer is invoked by substituting the Schmidt-number for  $Pr$ .

The literature reports a significant departure of  $Nu$  from the standard Graetz–Nusselt solution for  $Ra$  above 10<sup>4</sup>. The density gradient that occurs in the present system translates to a Rayleigh-number of  $Ra \approx 10^5$  for 2 mm capillaries and 30 mmol/l of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, which is strongly indicative of mixed convection. To further substantiate this hypothesis, the empirical solution (Eq. (9)) to the extended Graetz–Nusselt problem developed by Shome and Jensen [16] was applied to the present system (Fig. 8). The comparison shows an excellent rendering of the experimental results by the extended solution, which is a first confirmation of the present hypothesis. At the same time, this finding points the way to an improved experimental procedure: by reducing the dichromate concentration to 0.3 mmol/l and the capillary diameter to 1 mm, the Rayleigh-number can be lowered to  $\sim 4 \times 10^3$  which implies only insignificant natural convection.

$$Sh_m = 7.93 Ra^{0.21} \left( \frac{\nu_w}{\nu_b} \right)^{-0.05} \frac{\ln(1 + 0.13 \Delta)}{\Delta} \quad (9)$$

$$\Delta = Ra^{0.25} \left( \frac{\nu_w}{\nu_b} \right)^{0.5} Gr^{-0.5} \quad (10)$$

To further confirm the presence of natural convection and to test the improved experimental procedure, three sets of experiments were performed.

First, the capillary was placed in a vertical position with flow from top down. Under these circumstances, natural convection works in the same direction as the forced convection, which should lead to a lower enhancement of mass transfer as compared with horizontal flow.

Secondly, the dichromate concentration was reduced 100-fold to 0.3 mmol/l. This will reduce the copper concentration at the wall and thus the density gradient and natural convection accordingly.

Finally, the capillary diameter was halved to 1 mm, which reduces  $Ra$  eightfold and with it the strength of natural convection.

The results, summarised in Fig. 9, allow two conclusions. Firstly, the hypothesis that the observed deviation is caused mainly by natural convection is proven. This is best shown by the case of vertical flow, which differs from horizontal mode only in the direction of gravitational pull. This alone was sufficient to reduce the discrepancy significantly, which proves that mixed convection is a major cause of the observed deviation.

Secondly, it is shown that even after eliminating natural convection, the experiments do not coincide with

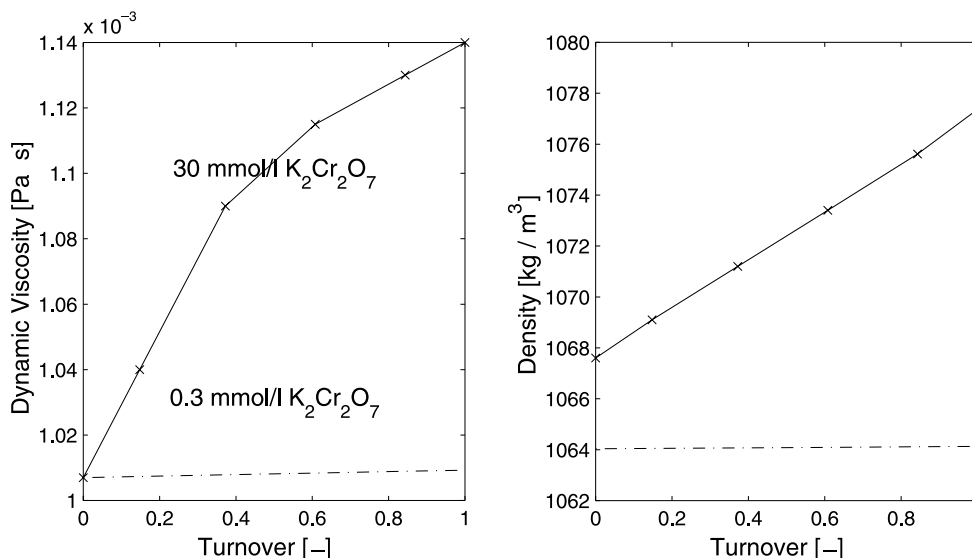


Fig. 7. Dynamic viscosity and density over  $\text{Cr}^{(\text{VI})}$  turnover at 25 °C for 30 and 0.3 mM initial  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1 M  $\text{H}_2\text{SO}_4$ .

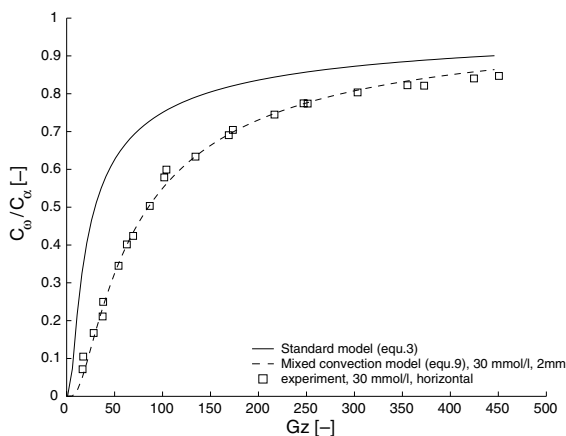


Fig. 8. Comparison of experimental data with theoretical solutions for forced and mixed convection. Correlations used are due to Stephan (forced, Eq. (3)) and Shome and Jensen (mixed convection, Eq. (9)). Experimental data based on 2 mm i.d. and 30 mM  $\text{K}_2\text{Cr}_2\text{O}_7$ , Graetz-number computed with  $D = 0.907 \times 10^{-9} \text{ m}^2/\text{s}$  tube.

theory. Application of the other techniques further reduces the discrepancy until the results for the dilute solution in 1 mm capillaries and in 2 mm vertical capillaries approach each other. However, a significant deviation from the standard solution remains. The close proximity of the results for vertical and horizontal operation using the dilute dichromate system and a comparison with the Shome and Jensen solution for mixed convection shows that under these circumstances natural convection is insignificant. Apparently the remaining deviation has a different cause.

The picture changes significantly after fitting the diffusion coefficient to the three mentioned experimental runs (Fig. 10), resulting  $D = 1.3756 \times 10^{-9} \text{ m}^2/\text{s}$ . The experimental data now coincide well with theory, with a standard deviation of 0.013.

This outcome again calls into doubt the diffusion coefficient reported by Gregory and Riddiford ( $D = 0.907 \times 10^{-9} \text{ m}^2/\text{s}$ ). This coefficient was measured at 30 mmol/l potassium dichromate, whereas we are now using a solution 100-fold more dilute. We therefore re-measured the coefficient by the Taylor-dispersion technique using both fresh dilute dichromate solution and solution to which copper sulphate was added. The results are summarised in Table 3 and show that dilution increases the diffusion coefficient, while the presence of small amounts of  $\text{Cu}^{(\text{II})}$  is without effect. The measured value of  $D$ , however, falls short of the value determined by fitting our data to theory.

At this point it is necessary to recall that  $D$  is not a true Fickian diffusion coefficient but an effective or apparent coefficient. It lumps the diffusivities and interaction coefficients of all the chromate and dichromate species in the system into one parameter. In addition, it also lumps any local change in the physical properties of the system into the same parameter. Using effective diffusivities cuts through the often intractable problems encountered in more rigorous modelling at the expense of generality. Newman [18, p. 304] points out that the effective diffusivity found for a chemically complex solution under one set of hydrodynamic and geometric conditions is not readily applicable to exactly the same solution under a different set of conditions. In the present case, the comparison of the copper dissolution and



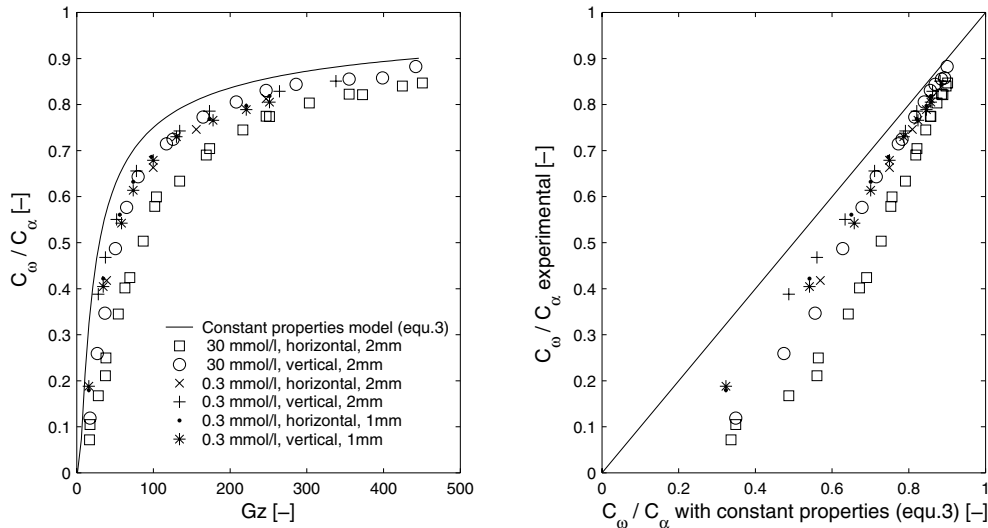


Fig. 9. Results from modified experiment, based on  $D = 0.907 \times 10^{-9} \text{ m}^2/\text{s}$ .

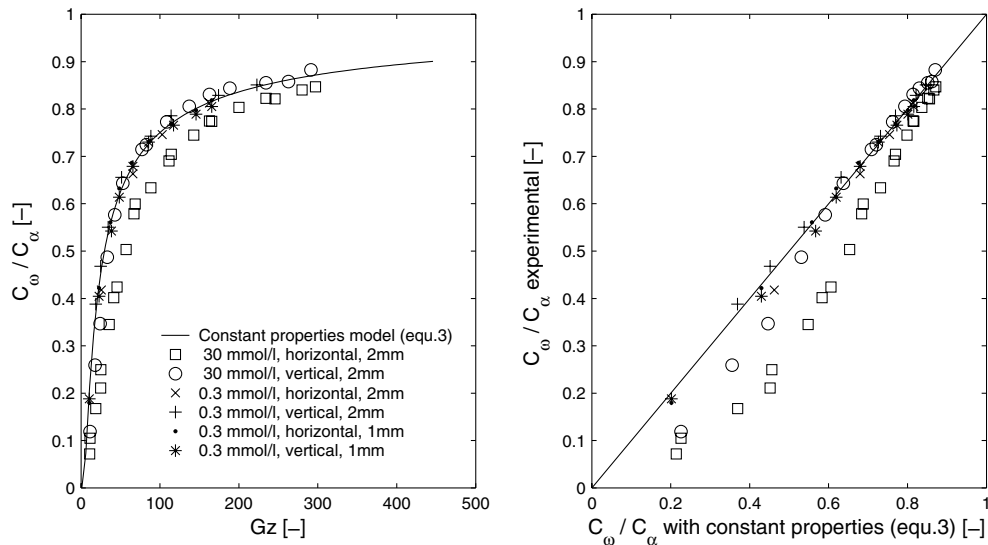


Fig. 10. Results from modified experiment as before, but based on  $D = 1.3756 \times 10^{-9} \text{ m}^2/\text{s}$ .

Table 3  
Diffusion coefficients fit to three experimental runs without natural convection

0.3 mmol/l $\text{K}_2\text{Cr}_2\text{O}_7$ in 1 M $\text{H}_2\text{SO}_4$	$D = 1.01 \times 10^{-9} \text{ m}^2/\text{s}$
As above with 0.9 mmol/l $\text{CuSO}_4$	$D = 0.99 \times 10^{-9} \text{ m}^2/\text{s}$

Taylor-dispersion experiments shows that different effective diffusivities apply to radial transport with and without the chemical reaction at the wall. This implicates the change in chemical composition and possibly also ionic interactions, such as migration and drag-effects which may result from the reaction, as the cause for the change in diffusivity.

Using the same analysis of the chemical composition as before, we found that the relative chemical composition of the dilute dichromate system does not change in the course of the reaction (Fig. 6B). This is quite plausible, since the strong background concentration of protons is hardly altered by the reaction of the dilute  $\text{Cr}^{(VI)}$  species. Therefore a shift to faster diffusing species can be ruled out.

### 3.2.6. Ionic interaction

Ionic interactions can occur in two different ways in the present system. On the one hand, the ionic double-layer at the copper wall may create a local electrical

potential which causes ionic migration. It is generally believed that such migration effects are suppressed by a high background electrolyte solution ([2,18, p. 332]). Gregory and Riddiford, however, observed an increase in effective diffusivity when they lowered the sulphuric acid concentration to 0.25 M [2] (see Table 2). They suggest ionic migration to be the cause, arguing that the strong background electrolyte concentration is depleted by the reaction near the wall, thus enabling migration. Whatever the merit of this argument may be, in the 100-fold dilute dichromate system the background electrolyte should be sufficient to reliably suppress migration.

Ionic drag appears to be a more plausible cause for the spread of diffusion coefficients. In the present system, the reduction of every  $\text{Cr}^{(\text{VI})}$  ion at the copper wall consumes seven protons. The resulting considerable proton flux to the wall may therefore cause a drag-effect on anions such as the  $\text{Cr}^{(\text{VI})}$  species, thus enhancing mass transfer to the wall. On the other hand, the strong concentration of background electrolyte may again absorb the drag-effect, since sulphate and hydrogen sulphate anions are approximately 1600 times more concentrated in the solution than the  $\text{Cr}^{(\text{VI})}$  anions. Diffusing protons are therefore  $\sim 1600$  times more likely to exert their drag on sulphate ions than on  $\text{Cr}^{(\text{VI})}$ .

To settle this argument, we can evaluate the effective ionic transport equation, which is defined by Taylor and Krishna [19, Eq. (2.4.33)] for a system containing  $n$  electrolytes without convection as

$$N_i = -D_i^\infty \nabla C_i + \frac{t_i}{z_i} \sum_{j=1}^n z_j D_j^\infty \nabla C_j \quad (11)$$

using the nomenclature in Table 4.

Using this definition, a simple numerical study was undertaken, in which a stagnant dichromate solution dissolved a flat copper wall. This one-dimensional problem was evaluated in Matlab using the above-mentioned method to impose the chemical equilibrium at every time-step. The process was run for 500 s (simulated time) and then evaluated. The results showed a considerable influence of ionic drag in the concentrated dichromate system, whereas there is no noticeable effect in the dilute system. Comparing the overall consumption of  $\text{Cr}^{(\text{VI})}$ , we find an increase of 10% for the concentrated and of 0.4% for the dilute system as compared to the simulation without ionic drag. On the basis of these findings, it appears unlikely

that ionic drag causes the observed change in diffusivity and its cause remains unexplained.

#### 4. Conclusions

There are three conclusions to be drawn from the analysis of the copper dissolution method.

Firstly, the observed discrepancy between theory and experiment in studying the Graetz–Nusselt problem with the copper dissolution technique can be attributed largely to natural convection caused by the build-up of copper sulphate near the capillary wall. The result is a mixed convection transport regime which displays an increased rate of mass transfer between liquid and wall as compared with the isochorous flow.

Secondly, natural convection can be largely suppressed by diluting the dichromate content of the feed solution while maintaining the same acidity as before. In this work, a solution containing 0.3 mmol/l dichromate was found to be unsusceptible to mixed convection.

Thirdly, even after eliminating natural convection, the experiments show a higher rate of mass transfer than predicted by theory. The cause of this error could not be elucidated. However, it can be eliminated by refitting the diffusion coefficient, which can be justified by the concept of effective diffusivity. Using a dilute solution and the new coefficient, the copper dissolution method performs well. Its behaviour can be described with a simple effective diffusivity model and the process of copper dissolution is entirely transport-controlled.

In view of our findings, the question arises why mixed convection was not observed on previous occasions when using the copper dissolution method. In the case of Gregory's and Riddiford's study of the rotating disk, the data correlated closely with the extended Levich-correlation, which is theoretically well founded. This implies that no mixed convection occurred. On reflection, this seems plausible. The rotating disk system is far less prone to mixed convection than laminar tube flow, because the region of the potentially highest density gradient close to the disk is simultaneously the region of strongest forced convection, which diminishes the density gradient. By contrast, in laminar flow, liquid at the wall stagnates, allowing the density gradient to build-up. Thus mixed convection probably did not occur in Gregory's and Riddiford's experiments.

In the case of other studies, the answer is less clear. For example, Zarraa et al. [5] studied mass transfer to a single sphere under gas sparging and Patil and Sharma [4] examined mass transfer in bubble columns with the aid of copper dissolution. In the absence of a reliable theoretical frame of reference, no deviation from theory could be detected and it thus remains unclear, whether mixed convection influenced their results or not. In such cases, the best approach may be to repeat the experiments

Table 4  
Nomenclature used in Eq. (11)

$N_i$	Molar flux of ionic species $i$
$D_i^\infty$	Diffusion coefficient at infinite dilution
$C_i$	Local concentration of species $i$
$t_i$	Transference number of species $i$
$z_i$	Charge of species $i$

at several degrees of dilution and to compare the results critically.

Finally, it should not be overlooked that mixed convection does not only inflict the copper dissolution method. On the contrary, it can potentially occur in most heat and mass transfer problems and then significantly affect the transport kinetics. The task is therefore not so much to exclude natural convection from experiments but to identify its presence and quantify its influence.

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