Risk of hydrocyanic acid release in the electroplating industry

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Abstract

This paper suggests assessing the consequences of hydrocyanic acid (HCN) release into the air by aqueous cyanide solutions in abnormal situations such as the accidental introduction of an acid, or the insertion of a cyanide in a pickling bath. It provides a well-defined source model and its resolution by methods peculiar to mass transport phenomena. The procedure consists of four stages: calculation of the liquid phase concentration, estimate of the HCN liquid–vapour equilibrium, determination of the mass transfer coefficient at the liquid–vapour interface, evaluation of the air concentration of HCN and of the damage distances. The results show that small baths operating at high temperatures are the major sources of risk. The building up of lethal air concentrations, on the other hand, is governed by the values of the mass transfer coefficient, which is itself determined by the flow dynamics and bath geometry. Concerning the magnitude of the risk, the fallout for external emergency planning is slight in all the cases investigated. © 2000 Elsevier Science B.V. All rights reserved.

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1. Electroplating processes

Electroplating is an electrochemical process used to cover an object with a thin layer of metal so as to change its surface properties and thus improve, for example, its

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appearance, mechanical, electrical and optical characteristics, and its resistance to corrosion.

Metals and their alloys are deposited by electrolysis of an aqueous solution of their salts. The objects to be coated are placed in an electrolytic cell and connected to the negative pole of a d.c. source to constitute the cathode. The anode, usually plates of the metal to be deposited, is connected to the positive pole. Electrolysis consumes these plates to replenish the solution of ions discharged onto the cathode.

Hydrocyanic salts are of major importance in the electroplating industry for the creation of thin coatings formed of fine crystals and with good anodic dissolution and throwing power. The main task of the cyanides is to keep the cations of the metal to be deposited in aqueous solution and sufficiently concentrated in the form of complexes [1–7].

2. Conditions for the formation of hydrocyanic acid (HCN)

Like all cyanides, HCN is a protoplasmatic poison. The cyanide ion combines with the enzymes that carry oxygen, inhibits cell activity and menaces vital functions. Its effects include myocardial arrest, respiratory paralysis and irreversible liver and kidney damage.

HCN toxicity in air is assessed according to the following parameter values [8–11]:

$$LC50 = 135 \, ppm; \, IDLH = 50 \, ppm; \, TLV\text{-}ceiling = 10 \, ppm.$$

Most safety regulations applying to electroplating shops using cyanides are directed to prevent any accidental contact between cyanide salts and acid solutions. This, in fact, will result in the formation of gaseous HCN:

$$CN^- + H^+ \leftrightarrow HCN$$

The probability of an event of this kind is regarded as extremely unlikely in the electroplating industry. It cannot be ruled out a priori, however, since pickling baths are often located near those containing cyanides for logistic purposes to ensure a regular, uniform flow of workpieces from one operation to the next.

Pickling prepares an object for electroplating by removing the layer of oxides usually present on its surface, so improving the adhesion of the coating, through the immersion in highly acid solutions of HCl.

The initial investigation was directed to the definition of two accident scenarios attributable to human errors:
(a) pouring of acids into a cyanide bath;
(b) insertion of cyanides in a pickling bath.

It was not thought necessary to consider mixing of the contents of a pickling bath with those of a cyanide bath, nor the breakage of both baths, since these events are ruled out by the fact that the baths must have a containing hollow space and their waste drain pipes must be isolated from each other.

This paper discusses two possible forms of accident a):

– regular operation of the ventilation device, failure of the plant employed to wash (abate) the gases routed to the chimney and emission of HCN to the atmosphere;

– failure of the local ventilation system and consequent dispersion of HCN into the area immediately surrounding the emission source.

3. Source model

In evaluating the risk associated with atmospheric releases of hazardous chemicals from various industrial activities, one of the main challenges is to estimate emission rates. This paper provides a source model and its resolution by methods peculiar to mass transport phenomena. The source model examine the accident scenario as a whole, from the first event to the consequences by means of simple but strict equations for each step. The results are compared to those got by equations extensively used in literature to evaluate the evaporation rate [12,13].

The calculation procedure consists of four stages:

(a) calculation of the liquid phase concentration;

(b) concentration of HCN at the liquid–vapour interface;

(c) determination of the mass transfer coefficient;

(d) calculation of the exhaust air HCN concentration.

Since the operating temperature and composition of electroplating baths vary considerably, the model was applied to two cases: silver plating, as an example of processes conducted at near-ambient temperatures; copper plating, as an example of those conducted at higher temperatures. Temperature is obviously a significant parameter as it influences the liquid–vapour equilibrium.

3.1. Concentrations of the species in equilibrium in the liquid phase

Accidental pouring of an acid into a cyanide solution results in local turbulence and diffusion movements. The greatest danger arises when all the CN^- ions are free in the solution. The complexes with the metal ions were thus regarded as completely dissociated. For a silver plating bath, HCN equilibrium concentration at 20°C following the addition of 37% HCl in the case of all the CN^- ions free in the solution has been compared to the one in which the $Ag(CN)_2^-$ dissociation equilibrium was considered: the two situations differs in small percentage. No account is taken of chemical kinetics and instantaneous establishment of a thermodynamic equilibrium is assumed.

The ion concentration at equilibrium in the liquid phase is determined by solving a set of equations: the mass balance equations, the equilibrium constant expressions and the charge balance. Calculation of the concentrations requires definition of the following working hypotheses.

(1) Concentration and amount of the acid introduced. As far as the concentration is concerned, one can set the addition of 37% HCl in mass or 98% H_2SO_4 as limit values. The addition of more diluted acids has less substantial effects. As to the quantity, the

later regulations require that cans of acids moved by hand should not contain more than few tens of litres.

(2) Solution volume to which the concentrations of the species in equilibrium in the liquid phase are to be referred. Assuming that the mixing of the mineral acid added involves the entire solution volume corresponds to the maximum hazard situation. Considering partial mixing in a confined solution volume, in fact, even though the HCl concentration will evidently be higher, because the corresponding area of emission is smaller, it can be shown that the emission rate is less than in the case of complete mixing. Take, for example, the introduction of 30 l of 30% HCl in a 300 l presilvering bath with a 0.5 m^2 surface and containing 2 g/l AgCN and 130 g/l NaCN. The mass transfer coefficient is 3e − 3 m/s and the delivery rate is 9e − 4 mol/s in the case of complete mixing. If, on the other hand, 30 l are added to a 30 l bath and these 60 l have a 0.1 m^2 surface, the delivery rate will be only 3e − 4 mol/s, i.e., one-third of the previous estimate.

(3) Bath volume. This varies from the few tens of litres used in craft operations such as silver plating to the tens of thousands of litres required for zinc plating.

Following the hydrolysis equilibrium:

$$CN^- + H_2O \leftrightarrow HCN + OH^-$$

the solution is buffered to a basic pH value, which means that very little HCN is in equilibrium with the other species. If the amount of acid added to the bath is not enough to cause a marked difference in the pH, the HCN concentration in the solution will not rise to dangerous levels. It can thus be asserted that if the amount of acid poured in is the same, small tanks are the sources of the greatest risk.

3.2. Concentration of HCN at the liquid–vapour interface

Determination of the HCN concentration in the liquid phase is followed by calculation of its concentration in air by application of Raoult's law to the binary mixture HCN–H$_2$0. The effect on the equilibrium of the ionic species in solution is thus ignored. This law provides a slightly conservative description of the binary system. Comparison with the experimental state diagram, in fact, showed that it slightly overestimated the HCN concentration in the vapour phase [7].

3.3. Determination of the mass transfer coefficient and of the exhaust air HCN concentration

Cyanide baths must be fitted with an exhaust system, usually set up by means of slits along their sides so as to leave their top surfaces free for the insertion and remove of the workpieces. A permanent exhaust system that remains in operation, even when the baths are not being used, is recommended.

The accidental case in which this local ventilation system is ineffective is ascribable to natural convection from flat horizontal surfaces.

Since the vapour phase components are HCN and H_2O, the solution–air mass transfer coefficient K_C was estimated by considering the lighter H_2O and applying the following correlation [14]:

$$St = 0.54(Gr \cdot Sc)^{1/4} \tag{1}$$

St and Gr are defined as:

$$St = \frac{K_C L}{D_{H_2O}} \tag{2}$$

$$Gr = \frac{L^3 \rho^2 g \zeta \left(m^i_{H_2O} - m_{H_2O} \right)}{\mu^2} \tag{3}$$

since

$$\zeta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial m_{H_2O}} \right) \tag{4}$$

In Eq. (3), the value corresponding to saturated air is used for $m^i_{H_2O}$ and m^i is taken as zero. D_{H_2O} values are estimated with an empirical correlation [15,16]. Table 1 illustrates the results in function of bath size and temperature.

When the ventilation system is working properly, a transverse velocity component imposed on the air above the bath draws off the fumes and prevents their diffusion into the work environment. The following correlation is used to calculate K_C in this case:

$$St \cdot Pr^{0.4} = 0.0287 \, Re_x^{-0.2} \tag{5}$$

since

$$St = \frac{K_C}{u_\infty} \tag{6}$$

$$Re_x = \frac{x u_\infty \rho}{\mu} \tag{7}$$

Assuming an exhaust system on both sides, consideration was given to one bath 0.5 m wide ($x = 0.25$ m) and another 1 m wide ($x = 0.5$ m). Application of the 0.25 m/s

Table 1
Mass transfer coefficients for the exhaust system failure case

Bath surface/perimeter [m]	Temperature [°C]	$1000 \times K_C$ [m/s]
1/6	20	2.77
	70	6.17
1/5	20	2.65
	70	5.89
1/4	20	2.51
	70	5.57
1/3	20	2.33
	70	5.19

Table 2
Mass transfer coefficients for the exhaust system operating case

Semi-amplitude of the bath [m]	Air speed [m/s]	$1000 \times K_c$ [m/s]
0.25	0.25	1.57
	0.50	2.73
0.50	0.25	2.73
	0.50	2.38

and 0.5 m/s values provided by relation (5) gives the K_C values shown in Table 2. These are of the same order of magnitude as those in Table 1.

Mass transfer coefficients foreseen for natural convention are always lower than those calculated for forced convection. The values given by Eq. (1) were thus regarded as overestimated and a reasonably prudent K_C value, namely $3e - 3$ m/s, was used for both natural and forced convection.

The calculation of the exhaust air HCN concentration can be simply done by dividing the HCN flow by the air flow. Table 3 shows the values of the minimum air flow to be removed in function of changes in the air speed and the size of the bath [1].

4. Examples

The nomograms in Figs. 1 and 2 show the exhaust air HCN concentration following the addition of a certain volume of 37% HCl to a silvering bath containing 80 g/l AgCN, 100 g/l KCN and 20 g/l K_2CO_3.

The x-axis of Fig. 1 illustrates the dimensionless ratio between this added volume and the initial cyanide solution volume. The corresponding concentration of HCN in equilibrium at the interface in the liquid phase is obtained in function of the temperature (20°C and 30°C). The HCN air concentration is then found by inserting this datum on the x-axis of Fig. 2 in function of the air flow.

Figs. 3 and 4 show the result of the same addition of HCl to a copper plating bath containing 50 g/l CuCN, 30 g/l KCN and 10 g/l K_2CO_3.

4.1. Failure of the abatement plant

Determination of the HCN concentration in the exhaust air was followed by consideration of an accident scenario, namely failure of the plant used to neutralise the air sent to the chimney.

Table 3
Minimum exhaust air flow rate

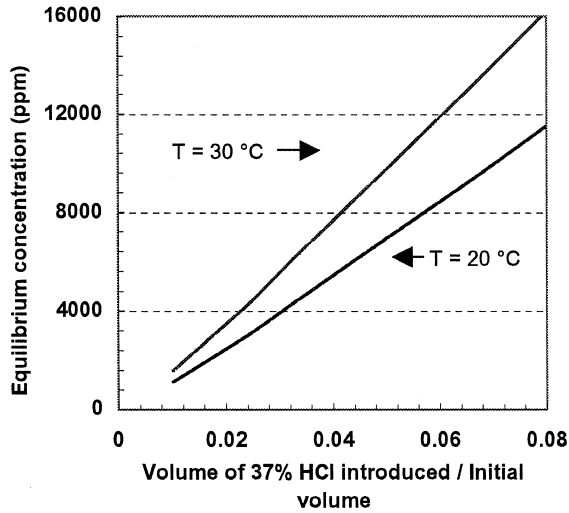| Bath width/length	Air speed [m/s]	Flow rate [m^3/s m^2]
1.0	0.25	0.6
	0.50	1.2
0.05	0.25	0.4
	0.50	0.8

Fig. 1. Silver plating: HCN concentration at the liquid–vapour interface in function of the ratio between the acid volume and the bath volume.

Several computer models are available to perform calculations and estimate hazard distances, but often they require extensive input data. Since the source model offers low values for the amount of HCN that may be released into the air by the electroplating baths, damage distances from the emission source were estimated with the Gaussian Plume Model (GPM) proposed by the TNO [17], which in general offers conservative results.
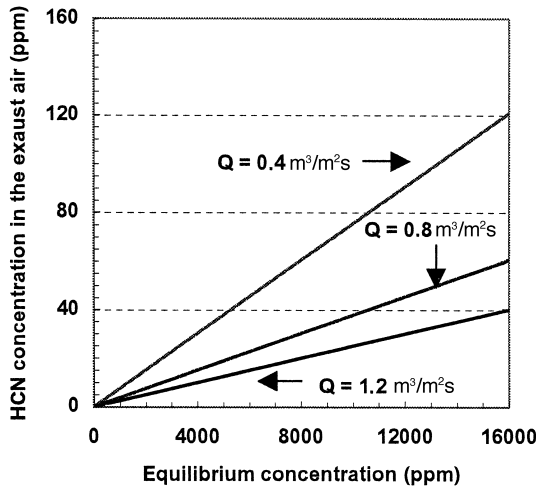

Fig. 2. Silver plating: HCN concentration of the exhaust air in function of the ratio between the acid volume and the bath volume.
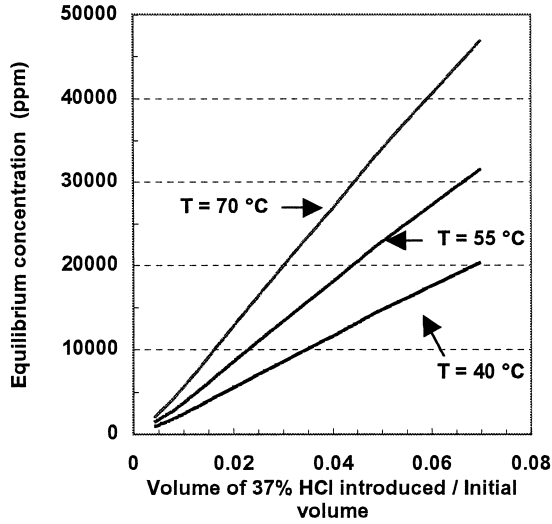
Fig. 3. Copper plating: HCN concentration at the liquid–vapour interface in function of the ratio between the acid volume and the bath volume.

C_i can range from about 10,000 to 50,000 ppm depending on the temperature and the ratio between the added acid volume and the initial bath volume. If we consider a bath with a surface of 2 m^2, we get two flow rates, namely $7e-5$ and $4e-4$ kg/s, both of which are less than the $1e-3$ kg/s minimum accepted as the initial datum by the
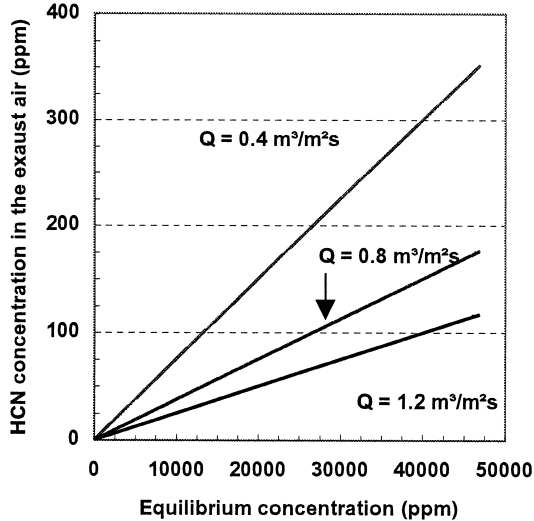

Fig. 4. Copper plating: HCN concentration in the exhaust air in function of the ratio between the acid volume and the bath volume.
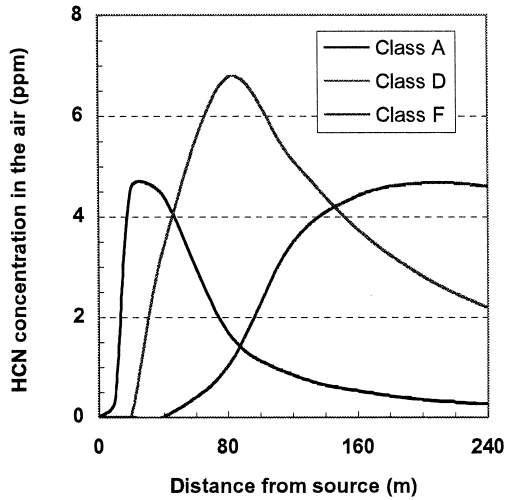
Fig. 5. Downwind concentration profiles at a man's height in function of atmospheric stability class.

program [17]. This minimum, itself a conservative value with respect to those calculated, was therefore adopted for the simulations. Application of commonly used equations [12,13] would give rates ranging between $3e-5$ and $1e-4$ kg/s, values similar to previous data.

Fig. 5 shows the results for an averaging time of 60 s assuming dispersion over flat ground (roughness class 1) for three atmosphere stability classes. Fig. 6 compares the concentration profiles for stability class D in function of changes in the roughness class. Lastly, Table 4 sets out the maximum sizes of the concentration contour, i.e. the area
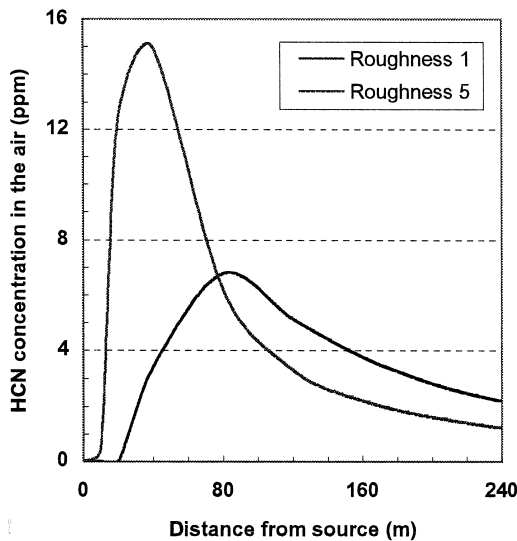

Fig. 6. Downwind concentration profiles at a man's height in function of roughness class.

Table 4
Dimensions of the concentration contour (10 ppm) and positions of the concentration peaks: flow rate 0.01 kg/s; wind speed 1 m/s

Stability class	Averaging time [s]	Roughness	Maximum distance [m]	Maximum amplitude [m]	Concentration peak [ppm]
F	60	1	1067	36	46 at 250 m
F	60	5	812	29	110 at 60 m
D	60	1	387	29	68 at 90 m
D	60	5	266	20	150 at 40 m
A	60	1	105	31	52 at 30 m
A	60	5	70	21	130 at 12 m
F	600	1	741	38	30 at 200 m
F	600	5	571	31	82 at 75 m
D	600	1	281	34	43 at 70 m
D	600	5	194	24	100 at 30 m
A	600	1	79	36	33 at 25 m
A	600	5	55	26	80 at 12 m

within which the concentration exceeds the TLV-ceiling (10 ppm), and the positions of the respective peaks. Due to the restrictions imposed by the program, an emitted flow rate of 1e − 2 kg/s, in other words two orders of magnitude greater than that calculated, was used for this simulation.

It can be concluded that in this second case, which is certainly the more critical, HCN concentrations higher than the IDLH at a downwind distance of less than 100 m are reached even when the most unfavourable atmosphere stability class is considered.

4.2. Failure of the local exhaust plant

If the exhaust plant fails, HCN contamination will initially affect the place where the accident occurs. The GPM is not appropriate for the description of dynamic diffusion in closed environments, as HCN vapours diffuses to the atmosphere through stagnant air. A strict solution is provided by integration of the mass balance equation with the three space coordinates and time, though this poses hard to solve difficulties. As a conservative approach, therefore, it was decided to render the problem unidimensional by considering continuous emission from a vertical flat surface towards a semi-infinite space instead of from a horizontal flat surface, as would be the case in real life. This assumption is prudent as it ignores the vertical diffusion component and regards the horizontal component as the only direction along which HCN can spread.

It is also supposed that the concentration at the interface is constant. This is a reasonable assumption, since the HCN flow is slight.

The situation can therefore be represented by the following differential equation [18]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{8}$$

which satisfies the boundary conditions:

$C = C_i$, for $x = 0$ and for $t > 0$

$C = 0$, for $x > 0$ and for $t = 0$

whose integral equation is:

$$C = C_i \text{erfc} \frac{x}{2\sqrt{Dt}}$$ (9)

Once the distance from the source is fixed, Eq. (9) is used to estimate the HCN concentration profile in function of time.

The estimated diffusion coefficient was increased to give $D = 2e - 4 \text{ m}^2/\text{s}$ for use in the calculations, since consideration is given to a global dispersion coefficient to take account of a convective component as well as the molecular diffusion [16].

It can be seen that the model envisages the attainment of C_i everywhere in space for long periods. The concentration profile for the first few minutes is thus significant.

Instantaneous establishment of a thermodynamic equilibrium is assumed. The calculations were made with regard to a distance of 1 m, since the release of HCN would first involve the operator who inadvertently poured the acid into the bath and would presumably still be close by.

Fig. 7 shows the concentration profiles when $C_i = 10,000$ and 50,000 ppm. It can be seen that in the second case the IDLH (50 ppm) is reached after 3 min. The lethal concentration is exceeded after 5 min, but is only reached after 8 min when $C_i = 10,000$ ppm.

It can thus be concluded that at first the accident only gives rise to a dangerous situation in the immediate vicinity of the bath and after a substantial period of time.
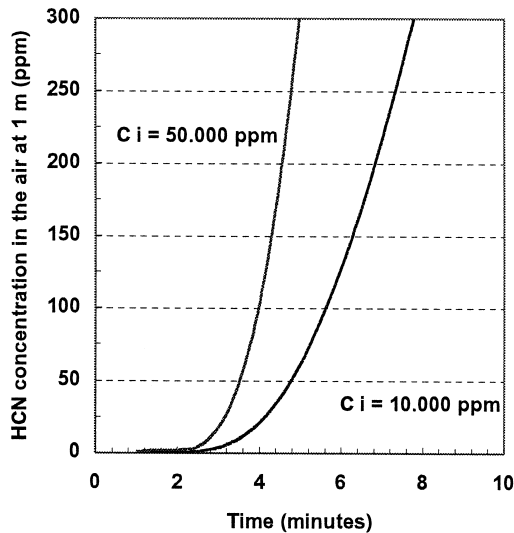
Fig. 7. Exhaust system failure: concentration profiles 1 m from the source.

Over longer times and greater distances, of course, the forecasts provided by the model would be less reliable.

5. Conclusions

This study proposes a source model for quantitative determination of the HCN that the cyanide solutions widely employed in the electroplating industry may emit in the event of the accidental introduction of acids through a human error.

The procedure consists of four stages: calculation of the liquid phase concentration; resolution of the liquid–vapour equilibrium, determination of the mass transfer coefficient at the liquid–vapour interface and calculation of the exhaust air HCN concentration. It was found that small baths operating at high temperatures are the major sources of risk.

The need for a strict source model arose from the observation that most risk analyses in electroplating operations simply assume that the amount of HCN that can be developed in the event of an accident is equal to the stoichiometric amount. The results provided by the method proposed show that these conditions are over-conservative and the fallout for external emergency planning may be very slight.

Notation

C	concentration in vapour phase, ppm
C_i	concentration at liquid–vapour interface, ppm
D	coefficient of diffusivity in air, m^2/s
g	gravity acceleration, m/s^2
Gr	Grashof number
K_C	mass transfer coefficient, m/s
L	characteristic length, ratio between the area and the perimeter of the bath, m
m	molar fraction in vapour phase
Pr	Prandtl number
Q	air exhausted per m^2 of free bath surface, $m^3/s\ m^2$
Re	Reynolds number
Sc	Schmidt number
St	Stanton number
t	time, s
T	absolute temperature, K
u_∞	control speed, m/s
x	space coordinate, m
μ	dynamic viscosity, Pa s
ρ	density, kg/m^3

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