AIR POLLUTION AND ENERGY EFFICIENCY

Turbulent acidic jets and plumes injected into an alkaline environment

The evaluation of the recovery rate of low pH discharges from EGCS SO\textsubscript{x} with respect to the requirements to measure background pH 4 metres from the overboard discharge point

Submitted by the Institute of Marine Engineering, Science and Technology (IMarEST)

**SUMMARY**

*Executive summary:* Resolution MEPC.184(59) 2009 *Guidelines for exhaust gas cleaning systems* (Guidelines) describes in paragraph 10.1.2.1 the discharged wash-water pH criteria. Paragraph 10.1.2.1 (ii) describes the setting of the ship’s side discharge pH limit based upon the recovery of the discharge plume to a pH value of 6.5 at 4 metres from the ship’s side. At least one previous measurement study has demonstrated rapid pH recovery of low pH wash-water discharge. The procedure to undertake the physical measurements, particularly with main engines running, is challenging and risky. Due to a number of ships likely to be retro-fitted with EGCS, the physical measurement process for certification requirements is likely to be a bottle neck to approvals. The University College London (UCL) has undertaken a study linking laboratory measured pH recovery with a theoretical pH recovery mathematical model. This paper validates the theoretical mathematical pH recovery model with actual accurately measured values under precise and controlled conditions.

*Strategic direction:* 7.3

*High-level action:* 7.3.2

*Planned output:* 7.3.2.1

*Action to be taken:* Paragraph 39

*Related document:* Resolution MEPC.184(59)
Background

1. The regulation requiring the use 0.1% sulphur fuel in sulphur emission control areas (ECAs) becomes mandatory from 1 January 2015. The use of Exhaust Gas Cleaning Systems (EGCS) for the removal of $\text{SO}_x$ in the exhaust gas is increasingly being adopted as an equivalent method as described in regulation 4 of MARPOL Annex VI.

2. Resolution MEPC.184(59) 2009 Guidelines for exhaust gas cleaning systems (Guidelines) describes in paragraph 10.1.2.1 the discharged wash-water pH criteria. Paragraph 10.1.2.1 (ii) describes a method of setting the ship’s side discharge pH limit based upon the recovery of the discharge plume to a pH value of 6.5 at 4 metres from the ship’s side. The development of the Guidelines took place at a time when there was limited detailed information on the performance of EGCS and the practical requirements for certification and approval. Paragraph 10.1.2.1 (ii) in the Guidelines acknowledges the acceptance of the mixing of the wash-water discharge with surrounding water to establish very rapid recovery of pH which is sustainable and with no consequent measurable harm to the aquatic environment.

3. At the time of the adoption of Resolution MEPC 184(59) there was only one operating EGCS. The unit was installed on the mv Pride of Kent, a vessel operating between Calais and Dover. A physical measurement experiment was undertaken on 21 September 2006 whilst the Pride of Kent was alongside in Dover harbour. The measurement using the standard and recognized conductivity, temperature and density probe (CTD) device (used by marine biologists) recorded that the recovery of pH, temperature and oxygen to near background levels was extremely short and within 2 metres from the ship. The following graph indicates one of the set of measurement records displayed in a three-dimensional matrix identical to the sampling positions used during the measurement experiment.

Introduction to the UCL study

4. The problem that UCL was asked to consider was the mechanism of the recovery of a low pH discharge into an alkaline environment and to establish and compare and confirm the empirical approach is in agreement with the experimental measurements. UCL was also asked to develop, using the confirmed empirical approach, a means of calculating the recovery of pH at 4 metres from the ship side in order to set a discharge limit pH at the ship’s side. This work has been completed and will be presented in a separate paper. The following
sections outline the work undertaken, the novel experimental methodology and the confirmation of the theoretical flow and mixing equations with actual measured values undertaken under controlled experimental conditions.

UCL study

Definition of pH

5 The Brønsted-Lowry definition (Brønsted 1923; Lowry 1923) of acids and bases states that acids are substances that donate hydrogen ions (H\(^+\)) and bases are substances that can add hydrogen ions. The pH scale, introduced by Sørensen (1909), is a measure of the concentration of H\(^+\) or OH\(^-\) ions on a logarithmic scale. At atmospheric pressure and 25°C a solution is considered acidic if pH < 7, neutral if pH = 7 and alkaline if pH > 7. The point of neutrality is temperature-dependant and varies from pH = 7.47 at 0°C, pH = 7 at 25°C and pH = 6.92 at 30°C. The effect of pressure on pH is negligible in the context of the marine environment addressed in this paper (Kitamura & Itoh 1987). It is important to note that the terminology of strong and weak in the context of acids/alkalis does not refer to their concentration but to their dissociation. In solution strong acids/alkalis dissociate fully into ions (H\(^+\) and the anion, A\(^-\), in the case of the acid, and OH\(^-\) and the cation, M\(^+\), in the case of the alkali). Weak acids/alkalis dissociate incompletely and the dissociation ratio at equilibrium is measured by a constant Ka for the acids and Kb for the alkalis (Gordus 1985).

Other applications of EGCS

6 Numerous air pollution control devices have been designed to mitigate the release of pollutants and to satisfy increasingly stringent environmental legislation. In areas where water is abundant (e.g. coastal regions, rivers or estuaries), numerous heavy industries (e.g. mining, chemical and power generation) use wet scrubbers to significantly reduce all of the aforementioned polluting by-products in exhaust gases. There are many types of wet scrubbers but they generally rely on the exhaust gas being brought into contact with water. The resulting exhaust gas wash-water contains sulphuric (H\(_2\)SO\(_4\)) and nitric (HNO\(_3\)) acids from the combination of sulphur and nitrogen oxides and water, particulates from incomplete combustion, and heavy metals. The wash-water is usually filtered of the particulate matter, which is stored in tanks, while the rest is discharged back into the natural environment. Due to the highly acidic nature of the wash-water, it needs to be diluted or treated prior to discharge in order to increase the outlet pH. Depending on the treatment, the discharge is usually in the form of a warm acidic turbulent plume because of the contact with hot exhaust gases. The depth, angle and rate of discharge are dependent on the individual configuration of the scrubber discharge pipe.

Buffering capacity of seawater

7 Seawater is a weak alkali buffer solution containing a large number of dissolved salts (Drever 1988), some of which influence its pH. Buffer solutions resist changes in pH when small amounts of strong acid are added by absorbing the H\(^+\) ions. The most important contributors for the sea are carbonate (CO\(_3^{2-}\)) and bicarbonate (HCO\(_3^-\)) ions that react with H\(^+\) ions in a reversible reaction to form carbonic acid that can in turn dissociate to form water and gaseous carbon dioxide (Frankignoulle 1994). Temperature, depth, coastal runoff and season all influence the buffering capacity of seawater. For instance, the melting of glacial ice in the summer introduces fresh water into seawater, which locally reduces the seawater buffering capacity. The seawater pH will always be lower at the free surface because of absorption of atmospheric carbon dioxide, resulting in the production of carbonic acid. There are also geographic variations to the chemical composition of sea and river water. For example, in the North Sea the pH of seawater varies from pH of 7.71 in Meyer Werft, Ems
River, Paneburg, Germany to 8.0 in Nassau harbour, Jade Bay, Wilhelmshaven, Germany (Behrends et al. 2005).

The impact of pH variation on marine organisms

Acids are not only very corrosive but some, such as sulphuric acid, are also toxic to marine life. Bell & Nebeker (1969) observed that most marine insects seemed to be able to tolerate an acidic environment with a pH of 5 for a 96-hour exposure time. However, when the pH was reduced to 3, the survival rate dropped significantly, with some species not surviving at all. Trent et al. (1978) investigated the effects of sulphuric acid on a range of marine animals and plants with various exposure times for up to 96 hours. They concluded that at a pH of 5, most organisms were able to survive the 96-hour exposure with varying mortality rates; however, snails were affected more than others and died rapidly. In an environment characterized by a pH of 3, all of the tested organisms except for midges and mosquito-fish died within a 24-hour exposure period. In the long term, a reduction in the average pH of seawater poses a significant risk to the local fauna, particularly to calcifying organisms with calcium carbonate shells and skeletons, as well as coral reefs (Raven et al. 2005). Acidic seawater dissolves these defensive properties, making them more vulnerable to predators.

Discharge plumes

To estimate the impact of scrubber discharge on the marine environment, it is important to evaluate how pH changes with distance from the point of discharge and how long aquatic animals spend in regions of depressed pH. This change depends both on dilution due to entrainment of ambient fluid, and on the acid-alkali reactions between the discharge and the ambient fluid. The dilution caused by entrainment at the edge of the jet/plume has been studied in detail over the last 50 years. Nevertheless, there is some debate about the detailed elements of entrainment, such as the dominance of nibbling versus engulfment (Hunt et al. 2006, 2011). Theoretical models on jets/plumes (List 1982) are usually based on the conceptual framework of Morton et al. (1956), which has been extended to include the effects of momentum, buoyancy and sources varying in time (Scase et al. 2006 a, b), non-Boussinesq behaviour (Woods 1997) and internal generation of buoyancy (Hunt & Kaye 2005). A number of studies have examined the chemistry of reacting jets/plumes. Conroy & Llewellyn-Smith (2008) analysed second-order irreversible exothermic and endothermic reactions between a point-source plume and a second species in the ambient fluid. Campbell & Cardoso (2010) and Cardoso & McHugh (2010) examined the influence of internal buoyancy generation through irreversible reactions resulting in phase change on the development of plumes in stratified and un-stratified environments. Cardoso & McHugh (2010) experimentally analysed a plume containing calcium carbonate particles descending in an acidic aqueous solution where the generation of carbon dioxide bubbles on the surface of the particles modified the buoyancy flux of the plume.

Use of dye indicators to establish neutralization point

The purpose of the UCL work was to study jet and plume discharges of acidic fluids into alkaline environments. This work analysed how the pH recovers back to its original value with distance and how this depends on the relative concentration of the acid and alkali. The theoretical models for jets and plumes have been studied in great detail (Woods 2010); however, there are gaps when considering the chemical reactions between an acidic plume and an alkaline environment. pH-sensitive dyes have been used before as visualization tools by Corriveau & Baines (1993) and Dimotakis & Brown (1976) to analyse mixing in turbulent jets. In the study by Corriveau & Baines (1993) it is assumed that the chemical reactions between the acid and the alkali happen very rapidly if the reactions are diffusion-limited, the
indicator responds rapidly at the point of neutralization and the acid and alkali undergo a sharp transition through the point of neutralization. The new part in the analysis is the combination of a fluid model with reversible acid-alkali reactions. In light of the discharge of wash-water from wet scrubbers into seawater, we limit our attention to Boussinesq flows.

Section 1.1 – The mathematical model

An acidic fluid issues with a mean vertical speed of \( w_0 \) from a circular orifice of radius \( b_0 \) into an otherwise stagnant ambient body of water. The injected fluid has a density \( \rho_a \) and contains a concentration \( C_{oa} \) of monoprotic strong acid HA. The ambient fluid has a density \( \rho_a \) and a concentration \( C_{ob} \) of alkali MOH. It is assumed that the issuing fluid is perfectly mixed across the width of the jet/plume. The analysis describes a purely acidic jet/plume injected into a purely alkaline environment. It can be straightforwardly extended to account for alkali in the jet/plume, as indeed is done to interpret experiments and apply analysis to practical situations. It is also assumed that the mixing processes have a far longer timescale than the chemical processes that happen very rapidly on timescales less than \( 10^{-9} \)s (Eigen 1954). For analytical simplicity, the present discussion is centred around strong monoprotic acids (e.g. nitric acid) which donate one \( \text{H}^+ \) ion per molecule. The limit of the acid being strong is in keeping with the practical context, although ambient fluid may be a weak alkali or dilute strong alkali.

Section 1.2 – Chemistry model

The first analysis is a strong acid and a strong or weak alkali reacting in an aqueous solution. Consider a fixed volume of acidic fluid \( V_a \) that is being diluted through the addition of alkaline fluid \( V_b \). The chemical reaction is governed by the conservation of charge:

\[
[H^+] + [M^+] = [OH^-] + [A^-], \tag{1.1}
\]

and the conservation of mass of alkali and acid respectively:

\[
C_{ob}^0 V_b = ([MOH] + [M^+])(V_a + V_b), \quad C_{oa}^0 V_a = [A^-](V_a + V_b). \tag{1.2 a, b}
\]

The square brackets denote the molar concentration (mol l\(^{-1}\)) of the species. The condition (1.2 b) occurs because the acid is strong and fully dissociates, i.e. \( \text{HA} \rightarrow \text{H}^+ + A^- \). Both water and a weak alkali dissociate reversibly, i.e. \( \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \) and \( \text{MOH} \rightleftharpoons \text{M}^+ + \text{OH}^- \). The dissociation constant of water \( K_w \) and alkali \( K_b \) are defined by:

\[
K_w = [\text{OH}^-][\text{H}^+], \quad K_b = \frac{[\text{M}^+][\text{OH}^-]}{[\text{MOH}]]. \tag{1.3 a, b}
\]

At 25°C and atmospheric pressure, \( K_w = 10^{-14} \text{mol}^2 \text{l}^2 \). In the standard notation, it is important to note that \( K_w \) and \( K_b \) have different units (mol l\(^{-1}\)) to \( K_w \), see, e.g. Atkins & De Paula (2006). Combining (1.1), (1.3 a) and (1.3 b) generates an implicit equation which relates the \( \text{H}^+ \) ion concentration to the dilution of the acid by the alkali:

\[
\frac{V_b}{V_a} = \frac{C_{oa}^0 - [H^+] + K_w/[H^+]}{C_{ob}^0/(1 + K_w/([H^+]K_b)) + [H^+] - K_w/[H^+]} = \mathcal{Q}. \tag{1.4}
\]
The fraction \( V_a/V_b \) can be expressed as the dilution factor \( D \). The pH of the resultant solution is defined in terms of the \( H^+ \) concentration:

\[
\text{pH} = -\log_{10}[H^+].
\] (1.5)

At neutralization \([H^+] = [OH^-]\) and from (1.4), the hydrogen ion concentration is equal to \([H^+] = K_w^{1/2}\), giving the dilution required for neutralization as:

\[
D = \frac{C_o^a}{C_o^b} \left( \frac{K_w^{1/2}}{K_b} + 1 \right). \] (1.6)

The two limits to consider are a strong acid–strong alkali and a strong acid–weak alkali reaction. A strong alkali is characterized by \( K_b/K_w^{1/2} \gg 1 \), and in this limit the hydrogen ion concentration is calculated from the quadratic:

\[
[H^+]^2 \left(1 + D\right) - (C_o^a - DC_o^b)[H^+] - (1 + D)K_w = 0. \] (1.7)

The quadratic equation can be solved for \([H^+]\) giving:

\[
[H^+] = \frac{1}{2} \left( \frac{C_o^a - DC_o^b}{1 + D} \pm \sqrt{\left( \frac{C_o^a - DC_o^b}{1 + D} \right)^2 + 4K_w} \right). \] (1.8)

When the reaction is far from neutralization and acidic (i.e. \((C_o^a DC_o^b)/(1+D) \gg K_w^{1/2}\)), the hydrogen ion concentration is:

\[
[H^+] \simeq \frac{C_o^a - DC_o^b}{1 + D}. \] (1.9)

Physically (1.9) shows that \([H^+]\) decreases due to the reaction (i.e. the numerator \(C_o^a DC_o^b\)) and the dilution (i.e. the denominator \(1/(1+D)\)). Beyond neutralization (i.e. \(DC_o^b>C_o^a\) and \([H^+] \ll K_w^{1/2}\)), the first term in (1.7) \( (H^+)^2 (D+1) \) is small compared with the last term and, therefore, equations (1.7) and (1.8) can be reduced to:

\[
[H^+] \simeq \frac{(1 + D)K_w}{DC_o^b - C_o^a}. \] (1.10)

For a weak alkali, characterized by \(K_w/[H^+]>K_b\), the balance in (1.4) reduces to:

\[
[H^+]^2 \left(1 + D + C_o^a DC_o^b/\overline{K_w} \right) - C_o^a[H^+] - (1 + D)K_w = 0. \] (1.11)

Figure 1 shows the pH variation of a mixture formed by titrating a strong acid against an alkali at 25°C. Figure 1(a) shows the case of a strong acid–strong alkali reaction for varying concentration of the alkali, where the concentration of acid is the same in each curve. The comparison between (1.9) (for \(pH < 7\)) and (1.10) (for \(pH > 7\)) is good and finally asymptotes to \(pH = -\log_{10}(K_w/C_o^a) = 14+\log_{10}C_o^a\). We see that close to neutralization the pH varies rapidly with \(D\). Figure 1(b) shows the strong acid–weak alkali reaction, the dashed lines correspond to (1.8) for \(pH < 5\) and (1.11) for \(pH > 5\).
Section 1.3 – Fluid flow model

A standard approach for modelling a turbulent plume is to consider how the mean flow velocity \( w \), radius \( b \) and density contrast between the plume \( p \) and ambient \( p_a \) vary with distance \( z \) from the source. The assumption of Morton et al. (1956, page 5, (2)) that the profiles are top-hat is applied, which is consistent with the recent work by Westerweel and others (Westerweel et al. 2005; Hunt et al. 2006; Westerweel et al. 2009), in which the conditionally averaged properties (velocity and concentration) (Bisset, Hunt & Rogers 2002) exhibit a large jump at the interface between the turbulent and non-turbulent regions. Averaging measurements over time provides velocity and concentration profiles which appear to be close to Gaussian in form, largely as a consequence of the random meandering of the interface between the turbulent plume and non-turbulent ambient fluid. Gaussian profiles have been the basis of many theoretical models as well (e.g. Jirka 2004) and are conceptually similar to the top-hat approach. The starting point is the conservation of momentum and mass (with an empirical closure for entrainment), which for a top-hat profile are given as:

\[
\frac{d}{dz} (\pi b^2 w) = 2 \pi \rho c w b,
\]

\[
\frac{d}{dz} (\pi b^2 w^2) = \frac{(\rho_a - \rho)}{\rho_0} g \pi b^2,
\]

\[
\frac{d}{dz} (\pi b^2 w_g \frac{(\rho_a - \rho)}{\rho_0}) = 0.
\]

The empirically determined entrainment coefficient \( \alpha \) in (1.12) shows some variation between plume and jet experiments. Kaminski et al. (2005) suggest that the enhancement of plumes is partly explained by the increase in baroclinically generated turbulence. Morton (1959) suggested that the entrainment rate should be related to the local level of turbulence, rather than to the mean flow. Turner (1969) noted that the resulting similarity solutions are not sensitive to the value of \( \alpha \); therefore, reasonably accurate solutions can be made on the assumption that they are constant. For this reason, it is assumed here that \( \alpha = 0.1 \) for jets and plumes; however, in the work of Hunt & Kaye (2005) it is suggested that this approach slightly underestimates the entrainment in the
plume. The system of equations can be re-expressed in terms of specific fluid momentum ($M = \pi b^2 w^2$), volume flux ($Q = \pi b^2 w$) and specific buoyancy flux ($B = \pi b^2 w (p_a - p)/p_0$) as:

$$\frac{dQ}{dz} = 2\alpha \pi^{1/2} M^{1/2}, \quad \frac{dM}{dz} = \frac{BQ}{M}, \quad \frac{dB}{dz} = 0. \quad (1.15 \ a, \ b, \ c)$$

Using the dimensionless variables, $Q = Q/\bar{Q}_o$, $M = M/M_o$, $B = B/B_o = 1$ and $\bar{z} = 2az/b_0$, the characteristics of the plume can be expressed as:

$$\frac{d\bar{Q}}{d\bar{z}} = \bar{M}^{1/2}, \quad \frac{d\bar{M}}{d\bar{z}} = \frac{4}{5} \Gamma_0 \bar{Q}/M, \quad (1.16 \ a, \ b)$$

where

$$\Gamma_0 = \frac{5B_0 \bar{Q}_0^3}{8\alpha \pi^{1/2} M_0^{5/2}}. \quad (1.17)$$

Here $\Gamma_o$ is a dimensionless measure of the relative strength of the initial buoyancy flux of the plume and can be used to classify the nature of the source, i.e. for jets $\Gamma_o = 0$, forced plumes $0 < \Gamma_o < 1$, pure plumes $\Gamma_o = 1$ and lazy plumes $\Gamma_o > 1$ (Hunt & Kaye 2001, 2005). The system in (1.16a,b) can be solved using the relationship:

$$\bar{M} = (1 + \Gamma_0 (\bar{Q}^2 - 1))^{2/5}, \quad (1.18)$$

between $\bar{M}$ and $\bar{Q}$. The volume flux $Q$ can be expressed implicitly in terms of the distance $\bar{z}$ from the source through:

$$\bar{z} = \int_1^{\bar{Q}} \frac{d\bar{Q}}{(\Gamma_0 (\bar{Q}^2 - 1) + 1)^{1/5}}. \quad (1.19)$$

For a pure jet source ($\Gamma_o = 0$), the radius and volume flux increase linearly with distance:

$$b = b_0 + 2\alpha z, \quad \bar{Q} = 1 + \bar{z}. \quad (1.20 \ a, \ b)$$

For $\Gamma_o > 0$, the asymptotic form can be obtained by writing (1.19), in the limit of $Q \to \infty$ asymptotic spread in the far field, accounting for the virtual origin:

$$b = b_0 + \frac{6}{5} \alpha z, \quad \bar{Q} \sim (\frac{3}{5} (\bar{z} - \bar{z}_0))^{5/3} \Gamma_0^{1/3}, \quad (1.21 \ a, \ b)$$

where the virtual origin is:

$$\bar{z}_0 = -\frac{1}{\Gamma_0^{1/5}} \int_1^{\infty} \left(\frac{1}{(\bar{Q}^2 - 1 + \Gamma_0^{-1})^{1/5}} - \frac{1}{\bar{Q}^{2/5}}\right) d\bar{Q} - \frac{5}{3} \Gamma_0^{1/5}. \quad (1.22)$$

When $\Gamma_o = 1$ and $\bar{z}_o = 5/3$, equations (1.21a,b) reduce to:

$$b = b_0 + \frac{6}{5} \alpha z, \quad \bar{Q} = \left(\frac{3\bar{z}}{5} + 1\right)^{5/3}. \quad (1.23 \ a, \ b)$$
Figure 2(a) shows the variation of $Q$ with $\bar{z}$ for a range of $\Gamma_0$ values. For $|\Gamma_0 - 1|/(Q^2 \Gamma_0) \ll 1$, the virtual origin can be approximated as:

$$\bar{z}_o \sim -\frac{32}{21 \Gamma_0^{1/5}} - \frac{1}{7 \Gamma_0^{6/5}}.$$

(1.24)

Figure 2(b) shows the variation of the virtual origin with $\Gamma_0$ and it can be concluded that (1.24) is a reasonable approximation for $\Gamma_0 > 0.2$.

Figure 2. In (a) the numerical volume of flux against distance for a range of $\Gamma_o = 0$ (dashed line), 0.1, 0.5, 1 (dotted line) and 2. In (b) the variation of the virtual origin $\bar{z}_o$ as a function of $\Gamma_o$ (1.22) (dashed line) compared against the analytical approximation (1.24) solid line).

The travel time of the fluid which is either formed as a part of the initial discharge or is entrained by the jet or plume from the point of origin to a distance $z$ is defined as:

$$\bar{t}(z) = \int_0^z \frac{dz}{w}.$$

(1.25)

Equation (1.25) is evaluated in a dimensionless form, $\bar{t} = 2aw_o t/b_o$, where:

$$\bar{t} = \int_1^{\bar{Q}} \frac{\bar{Q}}{\bar{M}} d\bar{z} = \int_1^{\bar{Q}} \frac{\bar{Q} d\bar{Q}}{(1 + \Gamma_0(\bar{Q}^2 - 1))^{3/5}}.$$

(1.26)

Again, there are two limiting cases of a pure jet ($\Gamma_o > 0$)

$$\bar{t} = \frac{1}{2} \bar{z}^2 + \bar{z}_o,$$

(1.27)

and for a plume ($\Gamma_o > 0$)

$$\bar{t} \sim \frac{5}{4} \left(\frac{5\bar{z}_o}{3}\right)^{4/3} \Gamma_0^{-1/3}.$$

(1.28)
17 Figure 3 shows the variation of travel time with distance and volume flux. The velocity in the jet decays as \( w \sim z^2 \) and in the plume as \( w \sim z^{1/3} \). Owing to the different rates of velocity decay, the travel time increases much more rapidly with distance from the nozzle for a jet than for a plume.

Section 1.4 – Combined chemistry and fluid-flow model

18 The concentration of acid in a jet or plume decreases with distance from the point of origin through the combination of dilution and chemical reactions. The mass conservation equations for the jet and plume are:

\[
\frac{d}{dz}(\pi b^2 w[A^-]) = 0, \tag{1.29}
\]

\[
\frac{d}{dz}(\pi b^2 w([\text{MOH}] + [M^+])) = 2\alpha \pi bwC_b^0, \tag{1.30}
\]

Figure 3: The numerical travel time against distance where \( \Gamma_0 = 0 \) (dashed line), 0.1, 0.5, 1 (dotted line) and 2.

The amount of acid within the jet or plume is described by (1.29) while (1.30) describes the increase in the alkali component within the jet or plume due to entrainment. The initial conditions at \( z = 0 \) are:

\[
[A^-] = C_a^0, \quad [\text{MOH}] + [M^+] = 0. \tag{1.31}
\]

The concentration of acid decreases due to dilution, where

\[
\dot{Q} = 1 + \bar{Q}. \tag{1.32}
\]

The solutions to (1.29) and (1.30) can be expressed in terms of volume flux as this determines the dilution of the acid and the increase in concentration of the alkali within the jet or plume, i.e.:

\[
[A^-] = \frac{C_a^0}{\dot{Q}}, \quad [\text{MOH}] + [M^+] = \frac{C_b^0(\dot{Q} - 1)}{\dot{Q}}. \tag{1.33 a, b}
\]
The terms in (1.33 a, b) are rearranged from (1.2 a, b) and are strictly valid for when the anion A is not present in the ambient fluid and the alkali in the ambient fluid has a uniform concentration of MOH. The condition for neutralization is stated in (1.6). The expressions for neutralization of a jet ($\Gamma_0 = 0$) can be obtained by combining (1.20b), (1.32) and (1.6), resulting in:

$$\tilde{z}_N = \frac{C_0^\alpha}{C_0^\beta} \left( \frac{K_m^{1/2}}{K_b} + 1 \right).$$

(1.34)

In the case of a plume ($\Gamma_0 > 0$), combining (1.21b), (1.32) and (1.6) results in:

$$\tilde{z}_N = \frac{5}{3} \Gamma_0^{1/5} \left[ 1 + \frac{C_0^\alpha}{C_0^\beta} \left( \frac{K_m^{1/2}}{K_b} + 1 \right) \right]^{3/5} + \tilde{z}_0.$$

(1.35)

Figure 4(a and b) shows the pH along the centreline in the jet and plume as a function of distance from the source, for the case of a strong acid injected into a strong alkali.

![Figure 4](image-url)
In the case when the concentrations of acid and alkali are both high, the results are insensitive to $\Gamma_0$ because the alkali solution is so strong that neutralization occurs close to the source. When the concentration of the alkali is reduced, neutralization occurs further away from the nozzle. As the neutralization distance increases, so does the momentum flux in the case of a plume, and that has a significant effect on increasing the neutralization distance. The variation of the pH in the acidic discharge can then be calculated by expressing $D = Q \cdot 1$ as a function of $\hat{z}$ and substituting this into (1.4) to determine $[H^+]$. The results for a strong acid injected into a weak alkali are shown in figure 4(c, d). Both the weak and strong alkalis increase the acid pH by the same amount in approximately the same distance, $\hat{z}$, up until a pH of 5. Far downstream, the pH of the discharge into a weak alkali solution has a minor dependence on $C_0^b$ than for the strong alkali case and a much lower pH.

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<th>$C_b^0$</th>
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Table 1. List of the chemical composition of the jet, plume and tank water. The dimensionless experimental neutralization distance $\hat{z}_N$ is measured from time averaged jet or plume images. The 100% buffer solution is created from 0.057 g l⁻¹ of sodium bicarbonate (molar mass 84 g mol⁻¹) and 0.163 g l⁻¹ of sodium carbonate decahydrate (molar mass 286 g mol⁻¹). The molar mass of sodium hydroxide is 40 g mol⁻¹. The molarity of London tap water was estimated to be $C_w = 0.0019$ mol l⁻¹ from the jet experiments and $C_l = 3.5 \times 10^{-5}$ mol l⁻¹ is the alkalinity of the litmus solution.

Section 2.1 – The experimental study

The purpose of the experimental study is to investigate the effects of the ambient alkaline fluid chemical composition and concentration on the neutralization distances of jets/plumes and to provide a comparison between the predicted points of neutralization and experimental observations. To reduce the number of variables in the experiments, we fixed
the jet/plume characteristics: acid type (nitric acid), acid concentration, flow rate and sodium chloride (NaCl) concentration in the case of the plume. The jets/plumes were generated by a hydrostatic head of water from a large header tank. Table 1 lists the substances used to increase the alkalinity of the ambient fluid.

**Section 2.2 – Experimental details**

22 The jet experiments took place in a wide rectangular tank with platform cross-sectional dimensions of 1.46 m × 0.97 m, filled to a depth of 0.46 m and illuminated by diffuse light sources from the bottom and along the length of the tank. In the case of the plume, the tank platform cross-sectional dimensions were 0.5 m × 0.5 m, filled to a depth of 0.66 m and illuminated by a diffuse light source from the side of the tank. The internal radius of the nozzle was fixed at $b_0 = 0.011$ m for the jet and $b_0 = 0.004$ m for the plume. A nozzle design for the plume was similar to the Cooper nozzle that is described in Kaye & Linden (2004). The flow rate for the jet at the end the nozzle was $Q = 1.31 \times 10^{-4}$ m$^3$/s. A dense plume was created by adding sodium chloride to a vertical discharge which does not play a role in the acid-alkali reactions. For the case of a plume, $Q = 2.53 \times 10^{-6}$ m$^3$/s, $\Delta \rho_0 = 36.59$ kg/m$^3$ resulting in $\Gamma_0 = 3.55$ at the end of the nozzle. The characteristic Reynolds number ($Re = 2b_0 w_0 / v$) for the jet is $Re = 7551$ and for the plume is $Re = 399$.

23 The neutralization distance of the jet/plume was determined optically from the litmus dye in the discharge. The significant quantities of water involved in these experiments precluded the use of distilled or deionized water; therefore, London tap water at a temperature of 19°C was used in all of the experiments. In the absence of any additional basic salts the jet neutralization distance was used to infer the concentration of dissolved salts in the tank ($C_0 w = 0.0019$ mol l$^{-1}$). The chemical characteristics of the tank water were changed by the addition of either a buffer salt combination, a single salt, an alkaline solution or an acidic solution. By adding alkali salts, the water became increasingly opaque to the point where the presence of the indicator could no longer be detected in the tank. This limited the shortest neutralization distance that could be observed. When additional basic salts were added then the total basic molar concentration in the tank was estimated to be the sum of $C_0 b$ and $C_w$, the molar concentration of the added alkalis and tap water.

24 All the experiments were recorded with a colour camera (Sony HDR-SR12E) at a resolution of 1920 × 1080 pixels, 24-bit colour depth and 25 frames per second. The videos were converted into a sequence of images at the video frame rate. A number of routines were written in Matlab R2012a using the image processing toolbox to gain either an instantaneous view of the colour intensity fields or a time-averaged measure. The averaged images were created over a time period of 7s. The images were split into red, green and blue colour components to gain a quantitative overview of how the colour intensity along the jet and plume centreline changed with distance from the nozzle. In the RGB colour model the colour intensity is within the range of 0 to 255 for each colour. The maximum colour intensity varies greatly depending on the opacity of the water in the tank; however, the relationship between the different colour components remains the same as distance from the nozzle increases.

25 Titration experiments were undertaken to examine how the pH and colour of the indicator dyes changed as acid reacted with an alkaline fluid. A diluted acid solution was created from a 1N standard nitric acid solution (Fluka Analytical) in distilled water and titrated against a sodium hydroxide solution in distilled water. The titration experiments involved increasing the volume of an initially acidic solution with an alkaline solution that was then stirred for a short period of time. The pH was measured using the Hannah Instruments HI 8428NEW probe two minutes after stirring. Litmus and universal indicator dyes were also
used to determine the pH from the colour of the solution. The reaction occurred in a Pyrex beaker, placed on top of a small diffuse light box.

Figure 5. The pH titration curves of nitric acid \((C_a^o = 0.0002 \text{ mol l}^{-1})\) against a sodium hydroxide solution of \(C_b^o = 0.01 \text{ mol l}^{-1}\) (dashed line) and distilled water \(C_b^o = 0 \text{ mol l}^{-1}\) (solid line). The solid and dashed lines show the theoretical predictions (1.4) while the symbols correspond to experimental data.

Section 2.3 – Experimental results – Titration experiments

26 Figure 5 shows the variation pH in a nitric acid solution as it is diluted with concentrated sodium hydroxide solution. The titration curve shows that when \(C_a^o\) is large, the pH changes rapidly through the point of neutralization. pH titration curves are affected by both chemical reactions and dilution. The titration of acid against distilled water \((C_a^o=0 \text{ mol l}^{-1})\) shows a change in the pH occurring wholly due to dilution. The pH in this case was measured with a pH probe. It is worth noting that the experiments involving distilled water are very sensitive to contamination.

27 Figure 6 shows how the colour of the litmus dye changes due to nitric acid being titrated against sodium hydroxide. As the amount of alkali added increases, the pH quickly passes through the point of neutralization and a corresponding rapid change in colour from red to blue is observed. Based on the colour intensity difference we are able to identify the point of neutralization.

Section 2.4 – Dilution and neutralization

28 The mixing in the jet was examined using litmus dye without the addition of acid and the results are shown in figure 7. The instantaneous image (a) shows a sharp edge to the jet/plume, but averaging over time (b), generates a smooth interface. The entrainment of packets of fluid from the edges of the jet/plume to the centre is characterised by a turbulent diffusivity which scales as \(D \sim \lambda wb \sim \lambda M^{1/2}\) where \(\lambda \sim 0.1\). The diffusivity remains constant for a jet while in the case of a plume it increases due to growth in \(M\). This means that the mixing at a fixed distance \(z\) from the nozzle is not instantaneous and explains why the edges are neutralised first and the centreline last. The distance between the concentration variation from the nozzle to point \(z\) along centre of the jet and from the nozzle to point \(z\) along the edge of the jet scales as \(D/w \sim \lambda b\). This is comparable to the local width of a turbulent jet/plume. The molecular diffusivity of the chemical species is typically very small \((D_{mol} \sim 10^{-9} \text{m}^2\text{s}^{-1})\). The concentration of filaments are of a scale \((D_{mol}L/u')^{1/2}\) where \(L\) is the integral scale and \(u'\) the root mean square velocity, which has a weak dependence on \(D_{mol}\) (da Silva et al. 2014)
The initial volume (200 ml) and alkalinity \( C'_w = 0.0014 \text{ mol l}^{-1} \) of the acidified solution increases through the addition of a fixed volume (2 ml) of alkali \( C'_b = 0.01 \text{ mol l}^{-1} \) at every step for 30 steps. The colour component intensity (dashed line - blue component; solid line - red component) of the pH sensitive dye, Litmus, varies and is highlighted at the following steps: step 4, pH \( \approx 3 \); step 13, pH \( \approx 4 \); step 14, pH \( \approx 7 \); step 15, pH \( \approx 10 \); step 27, pH \( \approx 11 \).

Figure 7: The blue colour component intensity for a jet experiment with litmus dye and no acid-alkali neutralization reactions, where (a) is the instantaneous image and (b) the time averaged image. The colour component intensity across the jet has been plotted along the vertical straight line.

An instantaneous image of an acidic jet is shown in figure 8(a) and quantitative view where the change from red (acidic) to blue (alkaline) occurs in a time-averaged jet is shown in figure 8(b,c). With distance from the nozzle the jet fluid becomes increasingly alkaline due to dilution and chemical reactions. Mixing between the ambient fluid and the jet or plume first occurs on the edges of the discharge where a gradual neutralization gradient is formed towards the centreline. The intensity of the blue and red colour components along the jet centreline are shown in figure 9. The cross-over point corresponds to the point of neutralization, distance \( z_N \) from the nozzle, but in the case that the lines cross multiple times, as seen in figure 9(b), the first point of contact is used. With increasing concentration of alkali salts in the ambient fluid, the neutralization distance \( z_N \) is reduced. It is necessary to take into account the influence of the dissolved salts in the London tap water. In the absence of any additional alkali salts added to the London tap water, the neutralization distance was measured to be \( Z_N = 17.9 \) in a jet, resulting in an alkali concentration of \( C_w = 0.0019 \text{ mol l}^{-1} \). The effective concentration of basic salts in the tank is estimated to be \( C_w + C'_b \). The alkalinity of the litmus dye in the discharge is denoted by \( C_l = 3.5 \times 10^{-5} \text{ mol l}^{-1} \). The total molarity of the acid in the jet and plume is given by \( C'_a - C_w - C_l \). The resulting molarity values were substituted into (1.34) for a jet and (1.35) for a plume to obtain theoretical predictions. Figure 10 show a comparison between the experimentally determined neutralization distance and theoretical predictions for jets and plumes respectively.
Section 2.5 – Practical estimates for acidic discharges into the environment

The model is applied to examine the pH of a buoyant vertical discharge into a river or sea. The chemistry of a strong acid reacting with seawater is more complex than the alkaline solution used in the experimental study due to a wide variety of dissolved salts in it. To closely mimic the typical reaction between an acid and seawater, a sample from the River Thames was titrated (taken a week before the Olympics at Embankment on Saturday, 21 July 2012 at 2 p.m.) and from Brighton Marina (taken on Saturday, 22 September 2012 at 2 p.m.). Both samples were taken on days where there was no rain.
The River Thames is a tidal river; however, at the point and time the sample was taken, the water was essentially fresh with suspended clay sediments. The River Thames water was used by the scrubber of the Battersea Power Station from 1925 to the 1960s where the discharge was supplemented with the addition of alkali agents. Figure 11 shows the variation of pH in an acidified samples of River Thames water and Brighton Marina water as they are diluted through the addition of unacidified River Thames/Brighton Marina water. 100 ml samples of river/seawater were acidified with 4 ml of 1 mol/l nitric acid resulting in pH = 3.27 for Thames water and pH = 3.45 for Brighton Marina. The pH at each stage of the dilution was determined by titrating a 10ml sample against a sodium hydroxide solution $C_b = 0.0233 \text{mol l}^{-1}$ in River Thames case and $C_b = 0.0210 \text{ mol l}^{-1}$ in Brighton Marina case. Litmus dye was used to determine the point of neutralization.

The main practical questions are what key variables control the neutralization distance and how much should the wash-water be diluted by prior to injection into the ambient water.
The subtle aspect is that dilution raises the initial pH but decreases the initial buoyancy flux of the discharge due to a reduction in temperature resulting in reduced entrainment by the plume. The density contrast between the discharge and the ambient can be estimated in terms of the temperature difference $\Delta T$:

$$\rho_0 - \rho_\infty = \gamma \Delta T,$$

(2.4.1)

where $\gamma$ is the thermal expansion coefficient of water that varies with temperature. The discharge characteristics are assumed to be pH = 3.27 and $T = 40^\circ C$ ($\gamma = 3.84 \times 10^{-4},^\circ\text{C}$). The ambient is assumed to have a temperature of $10^\circ C$ ($\gamma = 0.88 \times 10^{-4},^\circ\text{C}$) and the relationship between pH and dilution featured in figure 11. We are interested in an un-stratified environment where the plume is characterised by:

$$I_0 = \frac{5 \Delta \rho g \pi^2 b_0^5}{8 \alpha \rho_0 Q_0^2},$$

(2.4.2)

which is expressed in terms of parameters that would be part of any design procedure such as the discharge pipe radius $b_0$ and volume flux $Q_0$. The scrubber volume flux (quantity of water used to spray the exhaust gas) is proportional to the rate at which fuel is consumed in the engine and the fuel sulphur molarity. The volume flux of the discharge into seawater can be higher depending on how it is diluted (frequently various fluids such as engine cooling water are combined and discharged from one source).

Figure 12 shows the variation of the pH of an acidic discharge with distance when the wash-water has been diluted between 0 and 75%, for $b_0 = 0.2$ m and a discharge of $Q_f = 0.015$ m$^3$s$^{-1}$ from the scrubber. The value of $Q_0 = Q_f(1 + f)$ increases proportionally to the additional dilution ($f$) done prior to discharge. The relationship between $D$ and $\bar{z}$ is determined by solving (2.19) numerically and relating the dilution factor to the pH in the plume. The initial dilution has an effect of increasing the initial pH but decreasing the gradient of the pH with distance. In this configuration, the vertical neutralization distances are so large that pH recovery would certainly need to be supplemented with the addition of an alkaline agent.
Section 3.1 – UCL conclusions

34 A mathematical model was developed to analyse the characteristics of a monoprotic acidic jet or plume vertically injected into a stationary alkaline environment. Fundamentally, two processes were shown to be important: (a) dilution, caused by the mixing of acid with the alkaline ambient; and (b) chemical reactions. In the case of a strong acid and a strong alkali that have fully dissociated, the alkali tended to mop up the excess hydrogen ions after mixing, leading to a rapid reduction of the hydrogen ion concentration and a more rapid increase in the pH along the edges of the plume. At the point of neutralization the concentration of hydrogen ions and hydroxide ions is equal. A similar picture emerged for the case of a weak alkali where the hydroxide ions are only partially dissociated and as a result the pH showed a weaker dependence on the concentration of the alkali.

35 To provide support for these models, experiments on both the chemistry and fluid mechanical aspects were conducted. The chemistry model is consistent with the titration measurements. As was expected, for mixtures of strong acid and strong alkali, the pH changed rapidly around the point of neutralization. In contrast to the usual titration studies where the volume of fluid used for titration is often small, examined here are dilute strong alkalis where the pH changed much more slowly through the point of neutralization and the volume of the alkali was significant. Titrating a strong acid against distilled water shows that the pH rose by 1 unit when the acid was diluted by a factor of 10, except close to neutralization where the dissociation of H₂O is important.

36 The variation of the pH with distance from the outlet was examined using litmus indicator dye that was first calibrated against pH. The neutralization distance was measured from the colour component intensity variations along the centre line of the jet and plume. The measured neutralization distances (correcting for the alkalinity of the water) were consistent with the distances predicted by the analysis for a variety of acid and alkali combinations.

37 The results from this study were applied to provide predictions about the behaviour of strong acids when mixed with river and seawater. In this configuration, the pH as a function of distance, volume flux and discharge diameter were discussed. In the context of the environmental application to wet scrubber discharges from ships, when the ship is underway the discharges tend to be swept into the wake of the ship where dilution is extremely rapid. This alone will probably lead to the pH recovery even when the ambient fluid is fresh water. When a ship starts from rest or is in port, pH recovery occurs by both chemistry and dilution of the acid by entrainment. The engineering parameter which largely controls the pH recovery of a jet discharge is the diameter of the nozzle, where an initially small jet diameter significantly shortens the recovery distance. Since there are constraints on the exit flow rate (due to pressure head constraints and piping), halving the jet diameter (from 0.4 to 0.2 m) halves the neutralization distance. Further work is focused on exploring the policy constraints on wet scrubber discharges.

Conclusions

38 The UCL study has confirmed the theoretical mixing and buffering mechanisms of a low pH plume by comparison with measured experimental results undertaken under strictly controlled conditions. The study has confirmed the findings of ship-side measurements, including the measurements undertaken with the mv Pride of Kent, which show a rapid recovery of a low pH plume to background pH within less than 4 metres from the ship's side.

Action requested of the Committee

39 The Committee is invited to note this information.