Surface electrical discharges and plasma formation on electrolyte solutions

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\textbf{Abstract}

We report on microsecond pulsed high voltage capacitive discharges in salt water that are initially surface discharges but undergo a rapid transition to an arc plasma. We have observed and measured the speed of shock fronts and later arriving fluid pressure pulses due to the discharge pulse. In order to explain the large short time scale energy release leading to Mach 4–8 shock fronts and a transonic fluid pressure pulse, we postulate that they are detonation waves. We propose that very fast ionic reaction chemistries at high temperature and pressure are capable of producing such detonation waves. We also note that many others have observed a large energy release from short pulse salt-water discharges that they have been at a loss to explain.

1. Background

Over the past 25 years numerous experimental research papers have been published on discharges in salt water solutions; salt water “explosions”, for want of a better word [1–6]; and plasmoid formation (globules of plasma floating in the air) [7–11]. The experiments described in Refs. [1–11] all involved a pulsed capacitive discharge through water between the two electrodes, most likely surface discharges initially [12,13]. Most of the experiments used a prepared aqueous solution of electrolytes. Experiments [1–6] involved microsecond pulse lengths, small capacitors, and voltages in the 10s of kV range. The experiments were not well diagnosed but the authors observed the explosions and calculated their strength by measuring the impulse imparted to a projectile. Given the relatively small amount of electrical energy put into their devices, the authors were at a loss to explain the large short time scale energy release leading to Mach 4–8 shock fronts and a transonic fluid pressure pulse, we postulate that they are detonation waves. We propose that very fast ionic reaction chemistries at high temperature and pressure are capable of producing such detonation waves. We also note that many others have observed a large energy release from short pulse salt-water discharges that they have been at a loss to explain.

In 2006 several Japanese groups [8–10] began performing plasmoid experiments. In 2008 [11] a collaborative group from Holland and Germany published the results of similar plasmoid experiments with very extensive diagnostics.

Such experiments are very easy to implement. There are scores of videos of salt-water explosions on the Internet posted by amateur experimenters. Fig. 1 shows frames from videos that we made of such explosions. This particular experiment involved discharging a 450 \( \mu \)F capacitor at 2200 V across a 0.5 cm gap between small tungsten electrodes lying in a groove on an alumina surface. The amount of saturated salt water was about 10 \( \mu \)L. Only a small fraction of the capacitor charge was discharged through the salt solution. The total length of time involved was about 10 ms. The fireball is about 15 cm across with the emission most likely coming from Na\( ^+ \)(H\( _2 \)O), hydrated clusters, which emit from near the 589 nm atomic sodium D-line wavelength into the near IR [14] but with a smaller A-coefficient.

People have been performing such discharge experiments for more than a century. We know of no effort, however, to bring physical theory and computation to bear on understanding the processes leading to the observed phenomena. Much of the motivation for the plasmoid work has been due to the similarity between plasmoids and ball lightning [15,16]. Much may be learned from the ball lightning research that is relevant to the phenomenon being discussed here.

In Section 2 we will discuss our short pulse, high peak power surface discharge capacitive discharge experiments on salt water. We will concentrate exclusively upon aqueous NaCl solutions as...
many of the published experiments have used sodium chloride and because there is an abundance of basic physical and chemical data on such solutions.

In Section 3 we will discuss the hydrodynamics and plasma chemistry in the expanding region behind the shock front created by the discharge. This is the high temperature and high pressure chemistry of Na\(^+\) and Cl\(^-\) ions, electrons, air, and water.

2. Pulsed discharge experiments

2.1. Apparatus

Our device consists of a pressure cell having electrodes with a small salt-water reservoir between them in the bottom and a pressure transducer at the top. The two electrodes are connected across low inductance capacitors charged to 9–11 kV having a total capacitance of 0.75 \(\mu\)F. The discharge into the salt water was fired using a triggered air spark gap.

We recorded on a 100 MHz bandwidth Tektronix TDS 2014B digital oscilloscope \(V(t)\) across the electrodes using a Tektronix P6014 high voltage probe; \(I(t)\) in the circuit via a current divider, 20 dB attenuator, and Pearson 410 current monitor; and the output voltage from the pressure transducer and its circuit. Initially our experiments were performed in plasmas on the millisecond timescale, e.g. Fig. 1. Our pressure transducer, an Omegadyne PX-319300AI, has a sub-millisecond response time.

We used two electrode geometries and pressure cells of three different lengths. One cell has two vertical 6.35 mm diameter copper electrodes 1 cm long separated by 1.27 cm and is either 10 or 17 cm long. The other pressure cell has concentric electrodes and is 12 cm long. The inner electrode is copper with a 6.35 mm diameter. The outer electrode is stainless steel with a 12.7 mm inner diameter giving an electrode gap of 3.2 mm. The inside diameter of the PVC pressure cell is 5.7 cm.

Typically the volume of water used was between \(\sim 50\) and \(\sim 100\) \(\mu\)L having a maximum depth of about a millimeter. This allowed us to observe in the oscilloscope traces a surface discharge followed by a more conventional plasma arc discharge. We will discuss the physics and hypothesized chemistry of this below.

2.2. Experimental data

2.2.1. Preliminary experiments

We performed some experiments early on to estimate shock front speeds. In one set of experiments we placed a small length of aluminum foil across electrical contacts 10 cm above the discharge and measured on the oscilloscope the time between ignition of the discharge and when the fluid flow pressure wave opened the circuit. Sample digitized oscilloscope traces are shown in Fig. 2. The flow speed was transonic with a Mach number 0.9 \(\leqslant M \leqslant 1.6\) using the sound speed in air \(c_0 = 343\) m/s.

The sound speed in a gas is \(c = (\gamma p/\rho)^{1/2}\) where \(\gamma \equiv C_p/C_v\) is the adiabatic constant, \(p\) is the pressure, and \(\rho\) is the density, \(\gamma_{\text{air}} = 1.4\) but, as the mass of water in the cell was comparable to that of the air, \(\gamma\) may have a value of about 7/2, which would increase the value of \(c_0\). Not knowing the value of \(\gamma\) in the fluid flowing up from the discharge, we will always quote the Mach numbers with respect to the 343 m/s sound speed in air with the caveat that we do not actually know \(c_0\) in the fluid.

The second set of preliminary experiments was performed using a very small 1 mg rectangle of foil glued to a fine thread spanning the diameter of the open pressure cell. The thread acts as an under-damped torsion spring so that a laser beam reflected off the foil onto a masked photo-detector would merely be made to vibrate rapidly by a passing shock front of nanosecond width long before being blown off the thread by the later arrival of the trans- or sub-sonic fluid pressure wave. Fig. 3 shows a sample digitized oscilloscope trace from this measurement. These data indicate a shock speed of \(M \approx 8\) based on the sound speed in air. As the shock front is far ahead of the fluid wave, the air speed is appropriate.

2.2.2. Pressure transducer measurements

Due to using a pressure transducer of millisecond response time, as mentioned above, in experiments having microsecond characteristic times, there is no point in quoting absolute pressure changes. We were able, though, to measure shock and fluid pressure front transit times down to approximately 100 \(\mu\)s.

Fig. 4 shows a typical \(V(t)\) and \(I(t)\) oscilloscope trace showing the region of the surface discharge, its transition to a plasma arc discharge, and the oscillations due to the RLC circuit of the device. Fig. 4 also shows overlaid digitized oscilloscope traces from a different shot and vertical scale showing details of the surface discharge pulse. We will discuss in detail below how these waveforms come about. Hathaway et al. [5] displayed an oscillogram that is nearly identical to ours.
Fig. 5 shows $V(t)$ and $I(t)$ traces from shots made with the concentric electrode geometry in air, tap water, and a 3 M NaCl solution. The air traces show what would be expected of a typical high voltage spark across a small gap in air. The tap water shot shows the signature of the surface discharge. The traces from the 3 M salt solution show the surface discharge $V(t)$ signature distorted due to the very low resistance of the salt solution. The electrical energy deposited into the air, tap water, and salt water was, respectively, from $\int I(t)V(t)dt$, 11.1, 13.5, and 17.6 J. Most shots began with 9 kV $\leq V(t=0) \leq$ 11 kV. The energy stored in the capacitor was then 30–45 J. At least half the electrical energy was lost to the spark gap and the circuit.

In Fig. 6 we see signatures of Mach $\sim$3–4 shocks in the concentric geometry. These experiments were performed using a 3 M NaCl solution. Such shock wave signatures were not observed in air shots.

Fig. 7 shows the transonic fluid pressure front from several shots using a 3 M salt solution front in the long pressure cell and the good shot-to-shot reproducibility of the pressure signal. Air and salt water shots made using the concentric electrode geometry show the speed of the fluid flow pressure wave to be about 20% greater in the salt water discharge than in the air discharge. In addition, the gradient $dp(t)/dt$ of the leading edge of the front is thrice that of the air discharge.

Other reproducible features have been observed in our data that we are still pondering and analyzing. We did observe that Cl$_2$ gas is created by the discharge. When we opened the pressure cell we also found a moderately dense, cool, persistent aerosol fog within. Hathaway et al. [5] and Graneau et al. [6] photographed the formation of such an aerosol in open air shots using 10,000 and 35,000 frames per second (fps) framing cameras having 20–28 $\mu$s exposure times per frame.
From shock wave theory [17–19] for an instantaneous release of energy in space and time, i.e. \( E(t, r) = E_0 d(r/C_0 r_0) d(t/t_0) \), the shock front produced by 20 J of energy deposited in a point explosion would travel 10 cm in air in 750 \( \mu s \), 12 cm in 1.2 ms, and 17 cm in 2.8 ms, which are much longer than the times we observe given our \( \sim 18 \) J of electrical energy deposited in the salt-water.

Given that we do not deposit enough electrical energy to produce the observed shocks, even taking \( \int I(t)/V(t) \, dt \) as being deposited instantaneously, we need to look for an additional source of energy to drive the shock front. If we postulate that we have fast exothermic reaction chemistry in the fluid in the post ablation phase we can then explore the possibilities. Such chemical reactions, if they proceed rapidly enough, may produce a detonation front expanding outward from the plasma.

Given an energy deposition \( q \) ergs/g into a polytropic gas having adiabatic constant \( \gamma \), the speed of the detonation front, from the Zel'dovich–von Neumann–Doering (ZND) theory [18,20,21] is

\[
D = \left[ 2(\gamma^2 - 1)q \right]^{1/2} \text{cm/s}
\]

In the strong shock approximation. For \( \gamma = 1.4 \) and shock speeds of Mach 4 and Mach 8 this yields values of \( q \) equal to 1 and 4 kJ/g as being required neglecting energy dissipation. This amounts to approximately 18 and 72 kJ/mol taking most of the mass of the fluid to be that of water.

### 3. Models and analyses

#### 3.1. General picture

Due to space limitations we can do little more here than sketch out the physics and chemistry that we think underlie our experimental observations. A diagram depicting the geometry of our discharge experiments is shown in Fig. 8. Our simplified working model has most of the current initially between the electrodes being conducted near the surface of the electrolyte solution. With large applied voltages a thin layer near the liquid surface heats up very rapidly and ablates off, much like laser ablation of surfaces. This continues until the liquid is depleted or until an arc forms between the electrodes in the less dense ablated fluid. By then the salt water has become a dense mixture of \( H_2O(g) \) vapor; an aerosol of charged salt water drops of small diameter; free \( Na^+(g) \) and \( Cl^- \) ions; and free \( Na^+(aq) \) and \( Cl^- (aq) \) hydrated ionic clusters. Just what mix we have of these components and several additional possibilities as a function of time and vertical distance \( z \) depends upon the local values of the thermodynamic variables \( (T, p, \rho) \).

It is in this fluid between the high voltage electrodes that the physical and chemical processes take place over a period of less than about 30 \( \mu s \) leading to our observed data. This is a fluid rich in interesting physical and chemical processes.

#### 3.2. Surface discharge

It has been verified over the past two decades that the densities of anions and cations in an aqueous solution of electrolytes are substantially greater near an interface than in the bulk solution [22,23]. In a sodium chloride solution the \( Cl^- (aq) \) densities near the surface defined, say, by the Gibbs dividing line, are greater than the \( Na^+(aq) \) densities. Due to the greater ionic densities, weaker binding of the ions, and smaller fluid density near the surface we propose that the electrical conductivity \( \sigma \) due to ion transport at the surface \( z = z_s \) is much greater than the average value \( \langle \sigma \rangle \) in the bulk liquid. We might write the conductivity as \( \sigma(z) = \langle \sigma \rangle + \sigma_0 \delta(z - z_s) \). The current density is then \( j(z) = \sigma(z) E(z) \), where \( E(z) = V/\Delta x \) is the electric field between the electrodes with separation \( \Delta x \) and applied voltage \( V \).

The heating rate is

\[
dT(z)/dt = \sigma(z) E(z)^2 /C_r \rho(z) \times N_i(z)/\rho(z)^2 \tag{1}
\]

Due to the number density \( N_i(z) \) increasing in going from the depth of the liquid to the surface and the density \( \rho(z) \) decreasing simultaneously, \( dT(z)/dt \) is the greatest at the surface.
In modeling the ablation process we have made use of a 1-D self-similar hydrodynamic solution [24] and Van der Waal’s equation of state (EoS). Fig. 9 shows contour graphs of fluid density $\rho(z, t)$ at $t = 100$ ns and 1 $\mu$s. This particular calculation has 100 Lagrangian elements each of thickness 10 $\mu$m spanning a liquid depth of 1 mm. The blowing off of the surface layer in the $+z$ direction propels a rarefaction wave at sonic speed in the $-z$ direction into the liquid. Although the location of the “surface” is somewhat ambiguous after a short time, we have taken from a hydrodynamics perspective the surface as being that Lagrange element “d” that, at some time $t_d$ begins to move as the rarefaction wave reaches it.

Unless the salt water is too deep the ablation and surface process end when the rarefaction wave hits the bottom of the liquid. In the meantime, though, most of the electrical power goes into whichever element $d$, $1 \leq d \leq 100$ in this calculation, is the “surface”, at $t = t_d$. Since all elements have the same volume initially for $t \leq t_d$, if the energy depletion of the capacitor is not too great, $V(t)$, $I(t)$, and thus $P(t)$ remain approximately constant during the ablation phase. Hence we have the characteristic waveform of the surface discharge shown in Figs. 4 and 5. The ablation process will end as well when the leading edge of the expanding fluid becomes a more highly conducting plasma between the electrodes and the arc forms. This is why the Hathaway et al. [5] flat voltage pulse is only $\sim 2 \mu$s wide despite a water depth of more than 1 cm. As the rarefaction wave proceeds into the remaining salt water at about sonic speed it can be expected to splash an aerosol of salt-water droplets in the $+z$ direction. It has been known since the time of Rayleigh in the 1880s that such drops are electrically charged [25].

The speed of sound in water is 1484 m/s $\approx 1.5$ mm/$\mu$s. The speed in salt water is somewhat greater but, when the water has bubbles, dissolved gases, and other impurities, it is smaller. Generally, though, the time for the ablation of a film of water a millimeter or so thick is the microsecond time scales that we see in our data and also observed by others [5].

Fig. 10 shows a graph of the calculated $p(T)$ for a Lagrange element of the ablatting fluid over a period of about 100 ns without energy dissipation. $p(t)$ changes little and $p(T) \propto T$ on this timescale. The thermal conductivity of water is small so that the maximum possible heat flux across a water–air interface is only 223 W/mm² [26]. Fig. 10 also shows the density contours beyond the critical point of water, i.e. $p_c = 220$ atm and $T_c = 374$ °C, and the change in critical point with salt-water molarity [27]. Our results wherein $p(T) > p_{sat}$ for $T \leq T_c$ are comparable to the much more detailed hydrodynamics calculations of Grinenko et al. [28] for exploding wires in water. The water remains liquid into the supercritical region.

3.3 Post-surface discharge arc phase

Our working hypothesis has been that the ablated salt-water fluid expands up between the electrodes becoming less dense as it does so. For much of this time the fluid density is such that $p_{sat} \approx 10^{-3}$ g/cm³ $< p(z, t) < \rho_{water} \approx 1$ g/cm³. Ultimately the fluid density will change by about three orders of magnitude as it expands from liquid density to the density of the ambient air. If $T > 1400$ °C the fluid will consist of $H_2O(g)$ molecules and free Na⁺(g) and Cl⁻(g) ions. At higher temperatures there will be free electrons that have detached from Cl⁻ and even air and water dissociation and ionization products.

At temperatures $T < 1400$ °C, depending on density, a number of species may exist:

(1) Relatively high densities of $H_3O^+$ and $OH^-$ due to water self-ionization;

![Fig. 9. One-dimensional hydrodynamic calculation of the salt-water surface ablation process; 10 kV applied to 1 mm thickness of 5 M salt water.](image-url)
The plasma chemistry in the arc will be complex and remains the subject of continuing study. It is unlikely to be this simple but we might expect net exothermicity of the same order as this simple reaction scheme provides. Given that Faraday’s constant is 96,485 C/mol but the total charge on our capacitor is only about $7.5 \times 10^3$ C, it is unlikely that we are producing an explosive mixture of $H_2$ and $Cl_2$ via electrolysis.

The ionic reaction rates are very fast [31]. Above atmospheric density the rate coefficient is given by Langevin’s expression $k_{re} = 4n_e(\mu_+ + \mu_-)$ where the $\mu$ are the mobilities of the positive and negative ions. $\mu_+ \approx 0.1/\rho_0$, so that the rates decrease with density $\rho$ and increasing dielectric constant $\varepsilon_r$. The rates, though, are so large in the gas phase that they are still large even at a hundred times atmospheric density. At liquid density the dominant scattering mechanism is phonon scattering and ion mobilities tend to be larger than would be expected from the $(\rho_0 \mu)^{1/3}$ scaling.

The dielectric constant of water $\varepsilon(T, \rho)$ is ~78 for pure water at 25°C and 1 atm but is a strong function of temperature and density [32]. In addition, $\varepsilon_r$ decreases with increasing salt-water molarity [33]. There are considerable data on the properties of pure and salt water at high $T$ and $p$ available for our models and simulations. In addition to the dielectric constant we have high $T$ and $p$ electrical conductivity [34], thermodynamic properties [35,36], a very accurate equation of state for pure water [37], association/dissociation constants of salt water [34], and the dissociation constant of pure water $K_w(T, \rho)$ [38,39].

The dissociation constant of water is defined as $K_w = [H_2O^+][OH^-][H_2O]^2$ generally having units of (mol/kg)$^3$ or (molality)$^3$. For pure water at 25°C and atmospheric pressure $K_w = 10^{-14}$ from whence pH 7. $K_w(T, \rho)$ is graphed in Fig. 11. At the temperatures and densities in the region of $(p, T)$ space where our ablation $p(T)$ curve lies the mole fractions of the hydronium $H_3O^+$ and hydroxyl $OH^-$ may be in the range $10^{-4}$-$10^{-3}$. Consequently it appears that there may be substantial concentrations of $H_3O^+$ and $OH^-$ in addition to Na$^+$ and Cl$^-$ in the fluid at the temperatures and pressures shown in Fig. 10.

The rate coefficient for the recombination of $H_2O^+$ and Cl$^-$ yielding $HCl$ and $H_2O$ has been measured in atmospheric pressure flames [40] to have a value of $\sim 10^{-7}$ cm$^3$/s at even 2000 K, which is about 20 times the Na$^+$ + Cl$^-$ rate coefficient [31]. Recombination of molecular ions and clusters tends to have larger reaction rates than those for atomic ions due to tidal effects that enhance the process [41,42]. The exothermicity of the $H_2O^+ + Cl^-$ and Na$^+$ + OH$^-$ reactions together is 1206 kJ/mol $\approx 12.8$ kJ/g.

When we have substantial concentrations of the hydronium, hydroxyl, alkali, and halide ions at high temperatures channels then open up for the production of more complex and reactive ionic species such as ClO$^-$ and ClO$_3^-$ via, say, the intermediate HClO [43,44]. The chemistry may become very complex as there are numerous reactions known from radiological reactions [45], NaO$_2$ reactions from flame studies [46], and ClO$_3$ reactions from atmospheric research [47].

There appears to be sufficient chemical energy available via ionic reactions to produce strong detonation waves, which would explain our experimental results as well as those presented in Refs. [1–6].

4. Conclusions

Ionic plasma chemical reactions appear to have sufficient energy density and to be sufficiently fast, i.e. the power density is great enough, to drive detonation waves, beginning with a salt-water discharge.

The plasmoid experiments of Refs. [7–11], as with our early millisecond pulsed discharges (e.g. Fig. 1), are likely to be too slow compared to the hydrodynamic time scale for efficient production of intense detonation waves. Although we have no doubt that plasma chemistry occurs, we conjecture that the sodium emission that we see in Fig. 1 arises from the exothermic production of Na$^+$(H$_2$O)$_n$ hydrated clusters and their subsequent emission with A-coefficients much smaller than that of the atomic sodium resonance line. From our observations there appears to be considerable radiation trapping, which will decrease the effective A-coefficient.

Finally, the RF experiments of Roy et al. [48] produced what appears to be a flame on the surface of a salt water solution. It seems likely that the RF field employed in those experiments produced a surface plasma above which the Na$^+$ and Cl$^-$ ions hydrate, recombine, and the hydrated sodium clusters radiate as discussed above.

The ion and cluster chemistries outlined here are similar to the plasma chemistries proposed in recent years [15,16] to account for the ball lightning phenomena. We will present a detailed theory, models, and simulations of the processes outlined herein in a future publication.

There have been other experiments and analyses, both older and much more recent, on different systems that may have some relevance to our work.
In 1986 Radovanov et al. [49,50] published experiments and a plasma composition modeling for pulsed discharges in H2O/NaNO3 solutions. A discharge was created between electrodes immersed in the aqueous solution across a 6 mm gap with an applied voltage of 1.25–1.5 kV. The peak current was 3–4 kA having a pulse length of 20–40 μs and an energy deposition of 30–50 J. They measured a pressure of 20 bar 3 mm from the plasma channel. Using spectroscopic diagnostics they deduced electron densities on the order of 10^18 cm⁻³ and electron temperatures in the range of 16,000–18,000 K. Equilibrium calculations of plasma composition yielded electron and ion densities as functions of electron temperature for gas pressures to 100 bar. Using a fast camera they estimated the velocity of expansion of the plasma channel to be \( 4 \times 10^4 \) cm/s, which is transonic in a high pressure gas but subsonic in liquid water.

There has long been discussion in the scientific literature about the role that gas bubbles may play in the initiation and propagation of electric discharges in liquid water. The general consensus appears to be that gas bubbles play a significant role via either liquid evaporation from Joule heating or electrostatic expansion [51].

The experiments of Radovanov et al., as they take place in a conducting liquid, most likely involved Joule heating, as do our experiments, and did not involve pre-existing gas bubbles in the liquid. The electric fields are much too small for direct ionization of the components of the liquid solution. Zhao et al. [26] performed experiments and calculations using the Rayleigh–Plesset equation on the super heating and explosive vaporization of water on the microsecond time scale. We believe their results to be applicable to bubble and subsequent discharge formation in the Radovanov experiments. Exploding wire experiments are similar yet different in that, due to the nearly infinite conductivity of the wire compared to that of an electrolyte solution, the time scale is a thousand times shorter than that of the Radovanov et al. experiments. A gas “bubble” no doubt exists but it may be only a very thin sheath around the vaporizing wire.

Because our surface discharge occurs at the interface between the liquid and the ambient gas, i.e. a large pre-existing “bubble” if you will, the time scale is much shorter than that for experiments in liquid water but longer than the exploding wire time scale.

Very recent research on discharges within gas bubbles in liquids [52,53] has shown that the preferred discharge channel is along the interface between the gas and the liquid rather than across the bubble. As the dielectric constant of the liquid is reduced the streamers tend to propagate through the gas across the bubble. As the conductivity of the liquid increases the \( \varepsilon_r \) at which the transition between the two modes occurs decreases. As the electrolyte solution in our experiments is blown off and the fluid becomes supercritical, depending upon \((T, p, \rho)\) we have \( 1 < \varepsilon_r < 78 \).

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