nontoxicprint
Nontoxic Printmaking, Safe Painting & Printed Art

The basis of electro-etching:
a simplified explanation

CONTENT | SEARCH

by Alfonso Crujera & Bob Perkin

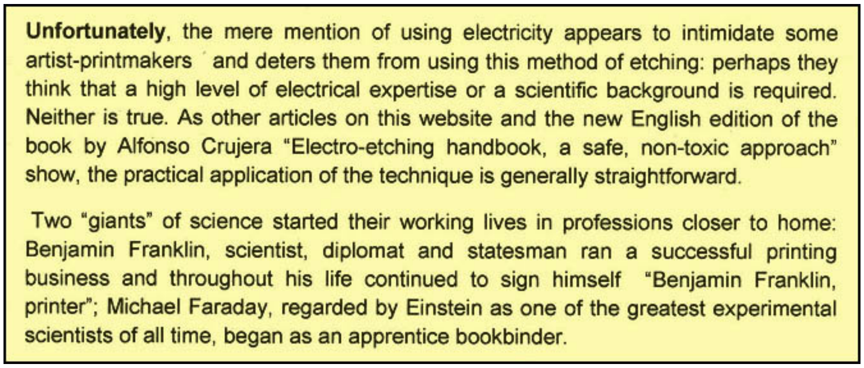
Electro Etching (by the same authors)

Introduction

Electro-etching, or “galv etch”, is an electrical etching technique which can be practiced conveniently and safely at home without the need for expensive equipment. For example, a copper plate 100 mm x 150 mm* prepared for etching in the usual way and with (say) a needled line image, can be etched using a single “AA” battery, another copper plate of a similar size, a couple of metal wires with connectors, an on/off switch, a plastic food container of around a litre capacity and an electrolyte - a liquid through which an electric current can flow, in this case some copper sulphate crystals dissolved in tap water.

To etch the copper plate, the two plates are held vertically in the electrolyte, facing one another and separated by about 50 mm. The battery and switch are connected between the two plates (electrodes), with the positive terminal attached to the plate which is to be etched and the negative terminal to the other copper plate; when the switch is closed electric current flows and etching takes place.

after Rembrandt



Unfortunately, the mere mention of using electricity appears to intimidate some artist-printmakers and deters them from using this method of etching: perhaps they think that a high level of electrical expertise or a scientific background is required. Neither is true. As other articles on this website and the new English edition of the book by Alfonso Crujera “Electro-etching handbook, a safe, non-toxic approach” show, the practical application of the technique is generally straightforward.

Two “giants” of science started their working lives in professions closer to home: Benjamin Franklin, scientist, diplomat and statesman ran a successful printing business and throughout his life continued to sign himself “Benjamin Franklin, printer”; Michael Faraday, regarded by Einstein as one of the greatest experimental scientists of all time, began as an apprentice bookbinder.

This article presents some of the underlying ideas and terminology connected with electro-etching. It is not crucial to understand these principles in order to produce successful etchings. However, we believe that by presenting a simplified explanation, it may remove some of the mystery of the technique and assist in encouraging its wider use.

Part 1 BACKGROUND

Following an introductory overview, some physical and chemical principles relevant to electro-etching are introduced. No prior knowledge is assumed and no mathematics is involved.

Basic kit for 'Home' electro-etching:

1 - power supply based on using rechargeable batteries

2 - inexpensive multi-meter to monitor electric current

3 - polymer containers holding electrolyte

4 - electrodes and connecting wire

5 - plates to be etched

6 - tape and clips for masking and attaching plates to anode electrode

7 - polymer container for holding equipment during etching

8 - dust mask, gloves, and safety glasses

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2. An overview of electro-etching

Essentially, the etching of the copper plate mentioned above is a result of the following electro-chemical process:

- Where the needled lines have broken through the ground, the surface of the copper plate is in contact with the liquid electrolyte;

- At these points of contact – the metal/liquid interface -and only at these points, the electrical energy obtained from the battery enables some of the copper atoms to give up their outer shell electrons to the copper plate;
- These copper atoms thereby become positively charged copper ions Cu++ which break away from the surface of the copper to become part of the liquid electrolyte;
- The amount of copper atoms which dissolve is proportional to the electric current flowing and the length of time the circuit is switched on.

The ionization and transfer of the copper atoms from the plate to the neighbouring liquid, described as “dissolution” by electro-chemists, corrosion by material scientists, is more easily recognized by us as etching.

For electro-etching copper, zinc and iron it is possible to use two plates of the same material with an appropriate electrolyte which has a salt of the same metal – copper, zinc or iron sulphate – in such a way that the electrolyte remains essentially unchanged with successive etchings. A similar approach for etching aluminium does not work.

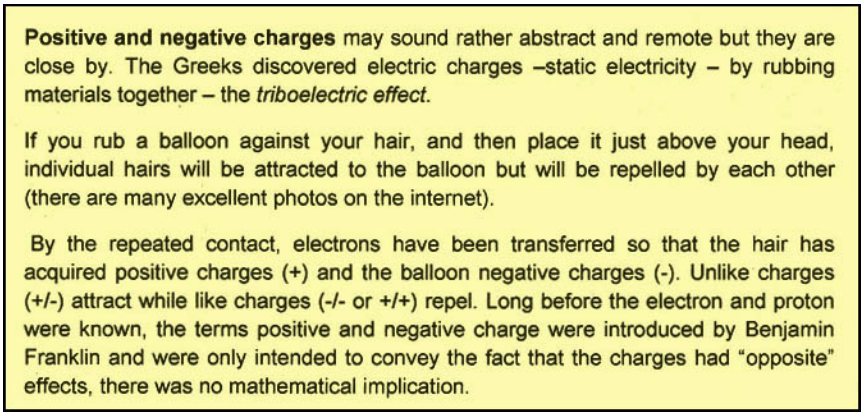
The key feature of electro-etching has been introduced: the atoms at the surface of a metal plate may give up some of their electrons to the external electric circuit to become positive ions which “dissolve” into the adjacent electrolyte. It now remains to fill in some of the details.

3. The material world – atoms and electrons

3.1 What we are made of – atoms; protons and electrons

Everything in the world is made from a combination of only a hundred or so substances, so-called elements, the majority of which are metals. The smallest amount of an element that can exist is an atom (from the Greek atomos “uncuttable”).

An atom is formed from just three sub-atomic particles, the proton, neutron and electron. The simplest atom belongs to the element hydrogen: it has a single electron orbiting around a nucleus consisting of a single proton. The proton possesses a “positive” electric charge while the electron has an equal but opposite “negative” charge so overall there is no excess charge –the atom is electro-neutral.

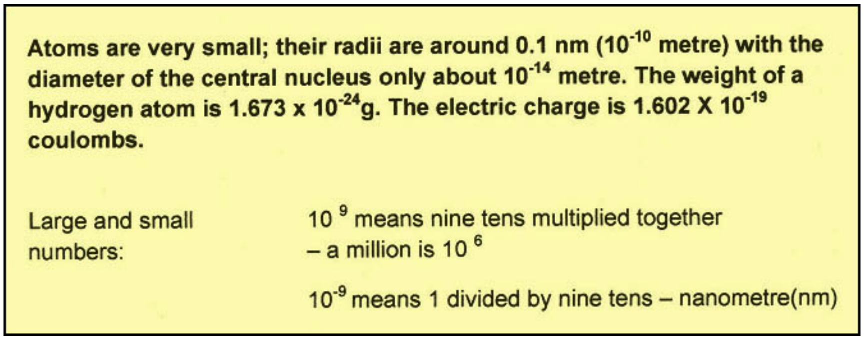


Positive and negative charges may sound rather abstract and remote but they are close by. The Greeks discovered electric charges –static electricity – by rubbing materials together – the *triboelectric effect*.

If you rub a balloon against your hair, and then place it just above your head, individual hairs will be attracted to the balloon but will be repelled by each other (there are many excellent photos on the internet).

By the repeated contact, electrons have been transferred so that the hair has acquired positive charges (+) and the balloon negative charges (-). Unlike charges (+/-) attract while like charges (-/- or +/+) repel. Long before the electron and proton were known, the terms positive and negative charge were introduced by Benjamin Franklin and were only intended to convey the fact that the charges had “opposite” effects, there was no mathematical implication.

The atomic structure of other elements can be built up from the basic hydrogen atom template by adding protons and neutrons to the nucleus and matching the number of protons by an equal number of electrons which orbit the central nucleus.



Atoms are very small; their radii are around 0.1 nm (10^{-10} metre) with the diameter of the central nucleus only about 10^{-14} metre. The weight of a hydrogen atom is 1.673 x 10^{-24}g. The electric charge is 1.602 X 10^{-19} coulombs.

Large and small numbers:	10^{9} means nine tens multiplied together – a million is 10^{6} 10^{-9} means 1 divided by nine tens – nanometre(nm)

3.2 The motion of electrons –orbits and shells

One way of visualizing an atom uses a "solar system model": the nucleus is the Sun and the electrons are the planets moving around the Sun in various orbits but with the difference that in a given orbit there can be more than one planet (electron). The permissible orbits and the number of electrons which can "occupy" a particular orbit or "shell" are governed by the rules of quantum physics.

Copper plate after electro-etching in copper sulphate; ground (candle wax) still on plate; dark areas: natural "electro-tint"

3.3 Outer sub-shells determine chemical properties

The chemical properties of an atom and the way it may interact and combine with other atoms to form molecules are largely determined by the number of electrons occupying the outer shells/sub-shells where the influence of the nucleus is less. Some elements, for example the gas argon, have atoms which have just the right number of electrons to completely fill one or several shells/sub-shells to give a stable, low energy structure, making them inert and unable to react with other atoms.

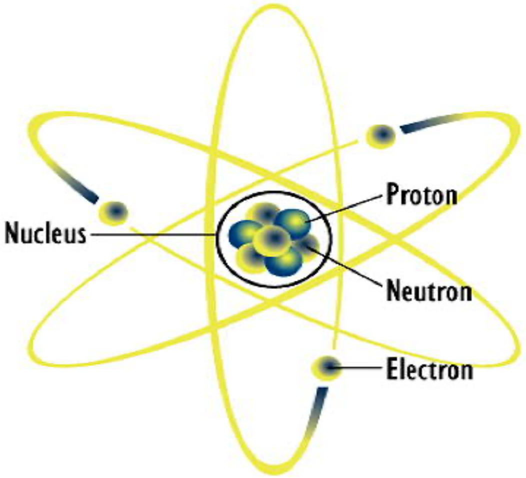


Figure 1: Rutherford “solar system model” of the atom, courtesy of Wikipedia article “Atom”

4. Metals

4.1 A basic property of metals

Characteristically, for metals the outer sub-shells will be occupied by only a few electrons, much less than the shell is able to accommodate. By contrast for many non-metals the outer sub-shells will be almost full of electrons.

4.2 A simple picture for the outer electrons within a metal – electric current

In a piece of metal there will be many millions of “outer” electrons which are essentially free to move within the open lattice, formed by the comparatively massive, immobile nuclei, and held together by the residue attractive electric forces between the “roaming” outer electrons and the nuclei. This may be pictured as a fixed array of buoys – the nuclei – bobbing on a “sea of electrons”. The passage of an electric current through a metal is really the flow of these electrons.

4.3 Sharing electrons and the formation of ions

Metal atoms would be more stable and “happier” if they had a structure similar to argon, that is, fully occupied shells/subshells. They can achieve this under the “right conditions” by donating their electrons in the outer sub-shells to a non-metal which correspondingly would like to gain the same number of electrons to complete its outer sub-shell so that it also has an argon-like structure.

> **Before the discovery** of the electron it was incorrectly thought by Faraday and Franklin that the flow of electric current was due to the flow of positive charge from the positive terminal of a battery, through the circuit to the negative terminal. This convention is still used today with the recognition that such a “conventional” current is equal and opposite to the actual electron current.

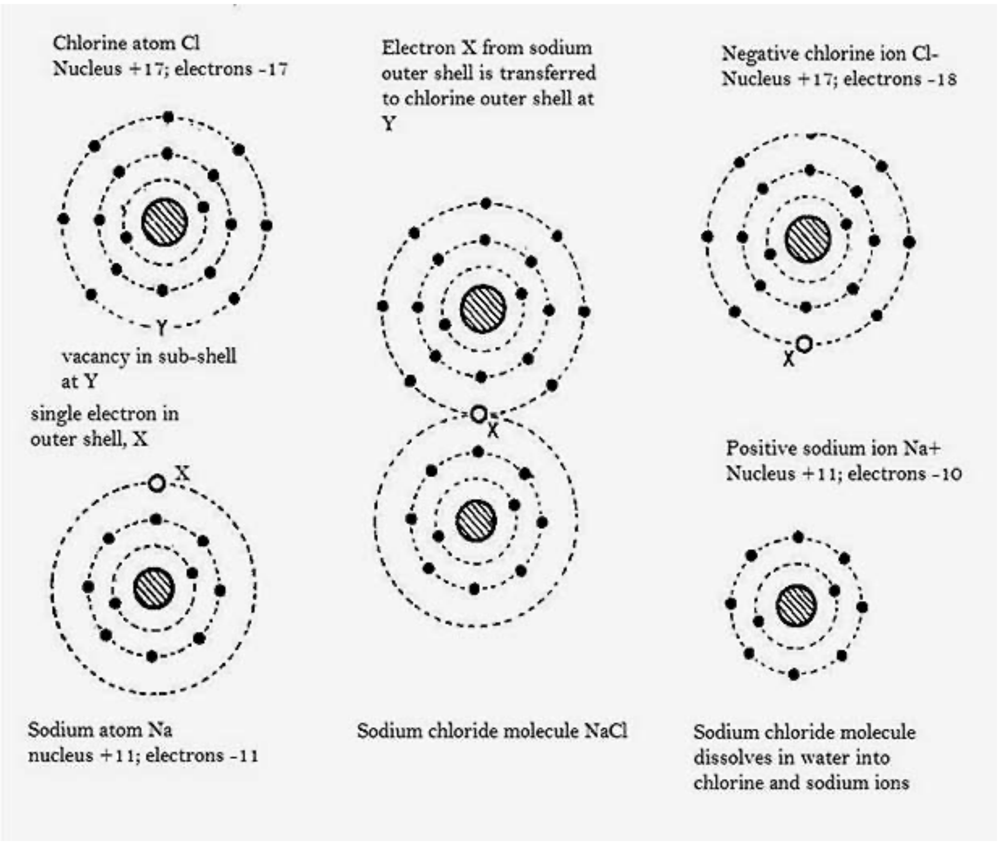


Figure 2: Formation of a sodium chloride molecule from sodium and chlorine atoms and the formation of chlorine and sodium ions by dissolving sodium chloride in water.

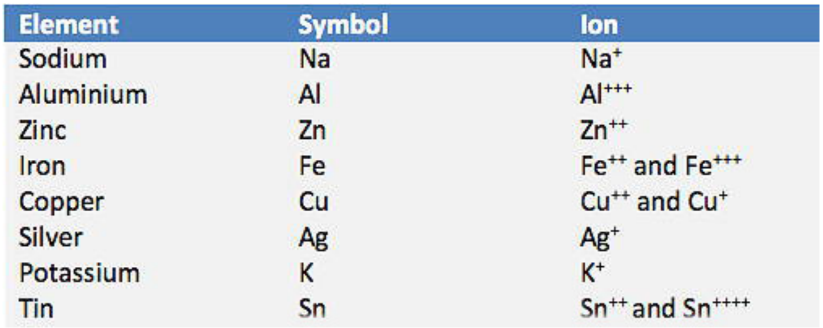
The atom of metallic sodium (Na) has its inner shells full leaving just one electron in its third shell - capable of holding eighteen electrons. The atom of the non-metal chlorine (Cl) again has its inner shells full, leaving seven electrons occupying the third shell, one electron short of filling two of its sub-shells.

By transferring an electron from the sodium atom to the chlorine atom both achieve complete sub-shells. The atoms Na and Cl become positively and negatively charged ions Na+ and Cl -.The electric force of attraction binds these ions together and leads to a lattice type structure incorporating huge numbers of atoms to give the familiar crystals of common salt.

A metal atom, in transferring electrons to another atom ceases to be a neutral atom - it has excess positive electric charge because there are more protons in the nucleus than there are orbiting electrons – it has become a positive ion. Similarly, the non-metal atom which has received the electrons now has excess negative charge, it has become a negative ion. The positive and negative ions thus formed become bound to one another through the attractive electric forces –*ionic bonding.*

4.4 Metals for etching and their ions

The electron distribution for atoms of aluminium, zinc, iron, copper –the metals of interest for etching -are such that the following ions would be expected if electrons in the outer shells can be lost to form a more stable ion:



Element	Symbol	Ion
Sodium	Na	Na^+
Aluminium	Al	Al^{+++}
Zinc	Zn	Zn^{++}
Iron	Fe	Fe^{++} and Fe^{+++}
Copper	Cu	Cu^{++} and Cu^+
Silver	Ag	Ag^+
Potassium	K	K^+
Tin	Sn	Sn^{++} and Sn^{++++}

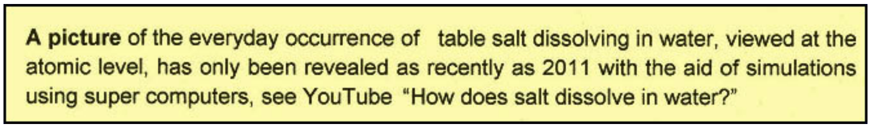
5. Electrolytes

5.1 Combining atoms - salts

Test print: line drawing, copper plate, candle wax ground,

electro-etch in copper sulphate; after Rembrandt

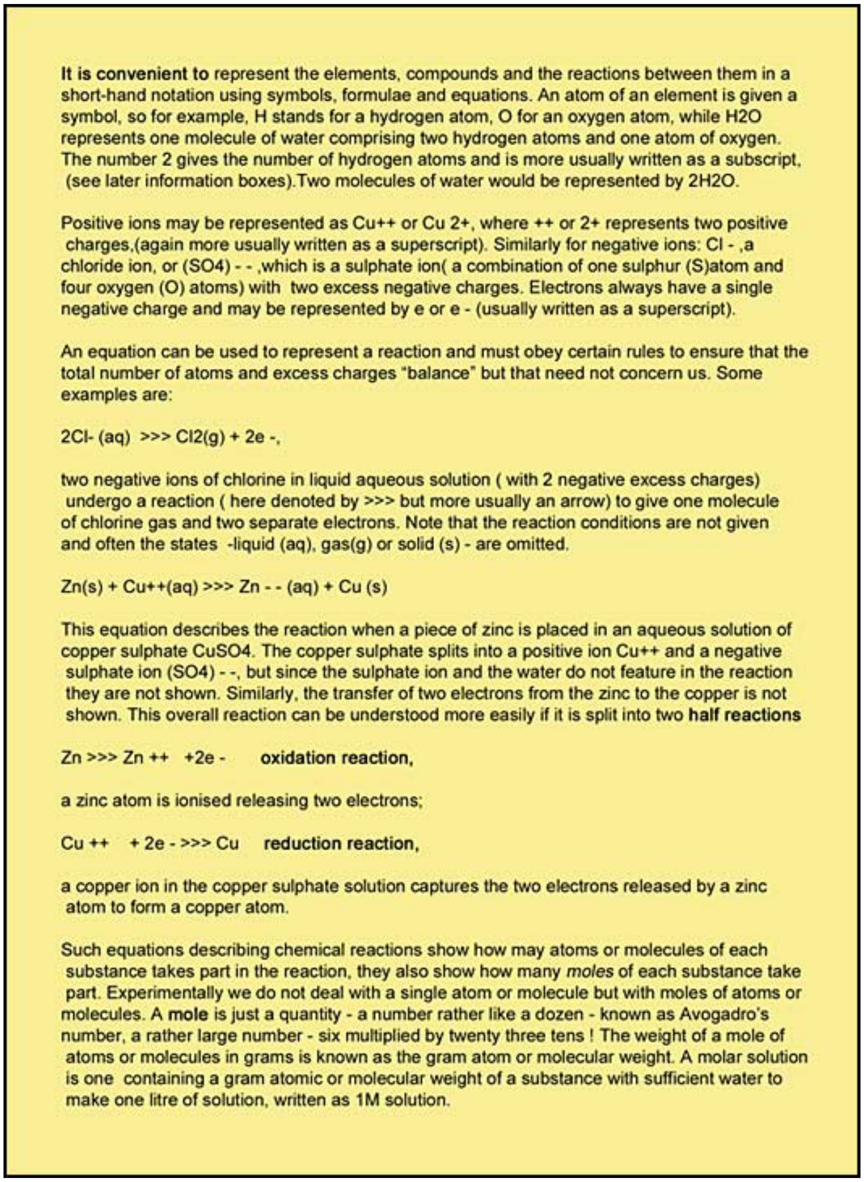
Elements seldom exist as single atoms, rather they combine to form compounds some of which consist of thousands of atoms. Of particular relevance for us are the compounds belonging to the class called salts, for example sodium chloride NaCl, common salt, copper sulphate $CuSO_4$ and iron sulphate $FeSO_4$ - each contains a metal atom and a sulphate molecule held together by ionic bonding. These salts are dissolved in water to form the liquid electrolytes for electro-etching.



A picture of the everyday occurrence of table salt dissolving in water, viewed at the atomic level, has only been revealed as recently as 2011 with the aid of simulations using super computers, see YouTube "How does salt dissolve in water?"

Your YouTube Video
will appear here.

Introducing chemical symbols and equations



It is convenient to represent the elements, compounds and the reactions between them in a short-hand notation using symbols, formulae and equations. An atom of an element is given a symbol, so for example, H stands for a hydrogen atom, O for an oxygen atom, while H2O represents one molecule of water comprising two hydrogen atoms and one atom of oxygen. The number 2 gives the number of hydrogen atoms and is more usually written as a subscript, (see later information boxes).Two molecules of water would be represented by 2H2O.

Positive ions may be represented as Cu++ or Cu 2+, where ++ or 2+ represents two positive charges,(again more usually written as a superscript). Similarly for negative ions: Cl - ,a chloride ion, or (SO4) - - ,which is a sulphate ion(a combination of one sulphur (S)atom and four oxygen (O) atoms) with two excess negative charges. Electrons always have a single negative charge and may be represented by e or e - (usually written as a superscript).

An equation can be used to represent a reaction and must obey certain rules to ensure that the total number of atoms and excess charges "balance" but that need not concern us. Some examples are:

2Cl- (aq) >>> Cl2(g) + 2e -,

two negative ions of chlorine in liquid aqueous solution (with 2 negative excess charges) undergo a reaction (here denoted by >>> but more usually an arrow) to give one molecule of chlorine gas and two separate electrons. Note that the reaction conditions are not given and often the states -liquid (aq), gas(g) or solid (s) - are omitted.

Zn(s) + Cu++(aq) >>> Zn - - (aq) + Cu (s)

This equation describes the reaction when a piece of zinc is placed in an aqueous solution of copper sulphate CuSO4. The copper sulphate splits into a positive ion Cu++ and a negative sulphate ion (SO4) - -, but since the sulphate ion and the water do not feature in the reaction they are not shown. Similarly, the transfer of two electrons from the zinc to the copper is not shown. This overall reaction can be understood more easily if it is split into two **half reactions**

Zn >>> Zn ++ +2e - **oxidation reaction,**

a zinc atom is ionised releasing two electrons;

Cu ++ + 2e - >>> Cu **reduction reaction,**

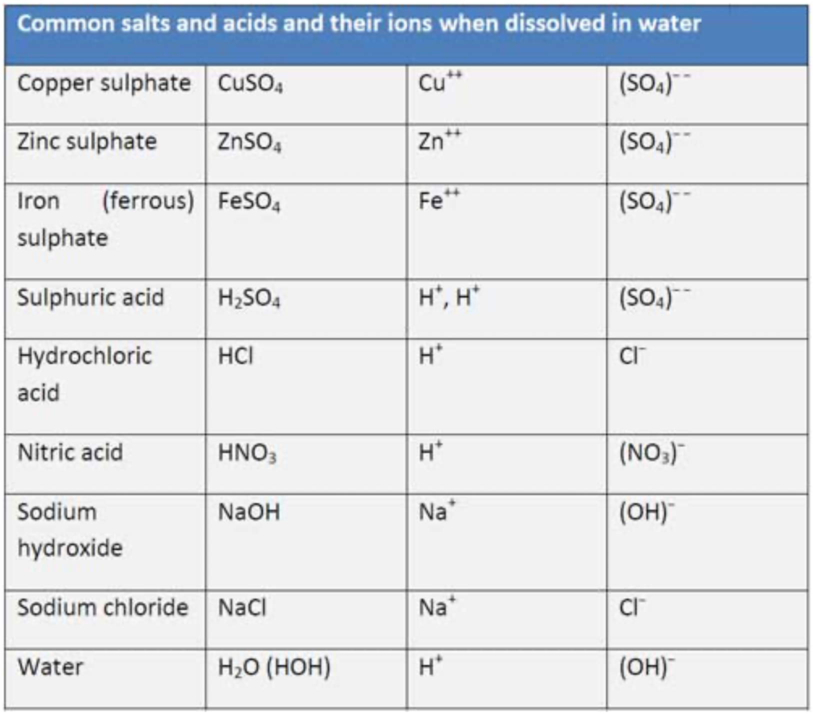
a copper ion in the copper sulphate solution captures the two electrons released by a zinc atom to form a copper atom.

Such equations describing chemical reactions show how may atoms or molecules of each substance takes part in the reaction, they also show how many *moles* of each substance take part. Experimentally we do not deal with a single atom or molecule but with moles of atoms or molecules. A **mole** is just a quantity - a number rather like a dozen - known as Avogadro's number, a rather large number - six multiplied by twenty three tens ! The weight of a mole of atoms or molecules in grams is known as the gram atom or molecular weight. A molar solution is one containing a gram atomic or molecular weight of a substance with sufficient water to make one litre of solution, written as 1M solution.

The weight of a mole of atoms or molecules in grams is known as the gram atomic or molecular weight. A molar solution is one in which the gram atomic or molecular weight of a substance is dissolved in one litre of water, written as 1M solution.

5.2 Dissolving salts in water: electrolytes for electro-etching; electro-neutrality

Salts dissolve in water because the water molecules are able to break up the ionic lattice into positive and negative ions. The number of negative and positive charges is equal so the solution as a whole is 'electro-neutral'- zero net charge.



Common salts and acids and their ions when dissolved in water			
Copper sulphate	$CuSO_4$	Cu^{++}	$(SO_4)^{--}$
Zinc sulphate	$ZnSO_4$	Zn^{++}	$(SO_4)^{--}$
Iron (ferrous) sulphate	$FeSO_4$	Fe^{++}	$(SO_4)^{--}$
Sulphuric acid	H_2SO_4	H^+, H^+	$(SO_4)^{--}$
Hydrochloric acid	HCl	H^+	Cl^-
Nitric acid	HNO_3	H^+	$(NO_3)^-$
Sodium hydroxide	NaOH	Na^+	$(OH)^-$
Sodium chloride	NaCl	Na^+	Cl^-
Water	H_2O (HOH)	H^+	$(OH)^-$

A general principle is that nature, left to itself, discourages processes which create excess electric charge, it prefers electro-neutrality.

5.3 Electric current in a liquid electrolyte; salt bridge

In an electrolyte there are no free electrons to provide the electric current. Instead the current is due to the movement of the positive and negative ions. For current to flow from one container of electrolyte to another, a salt bridge may be used.

A salt bridge is typically an inverted glass U-tube with each end dipping into one of the containers. It is filled with an appropriate electrolyte with porous plugs at each end. These plugs allow the ions from the electrolyte in the salt bridge to pass through into the containers but prevent the ions in the containers from flowing into the bridge; see the later image of the Daniell cell.

PART 2 ELECTRO-ETCHING

Using the information from Part 1, the basics of electro-etching are introduced.

6. Metal plates immersed in electrolytes –towards electro-etching

6.1 A zinc plate in zinc sulphate solution

If a plate of zinc is placed in a beaker containing a solution of zinc sulphate – a "zinc half- cell" - outwardly not much appears to happen.

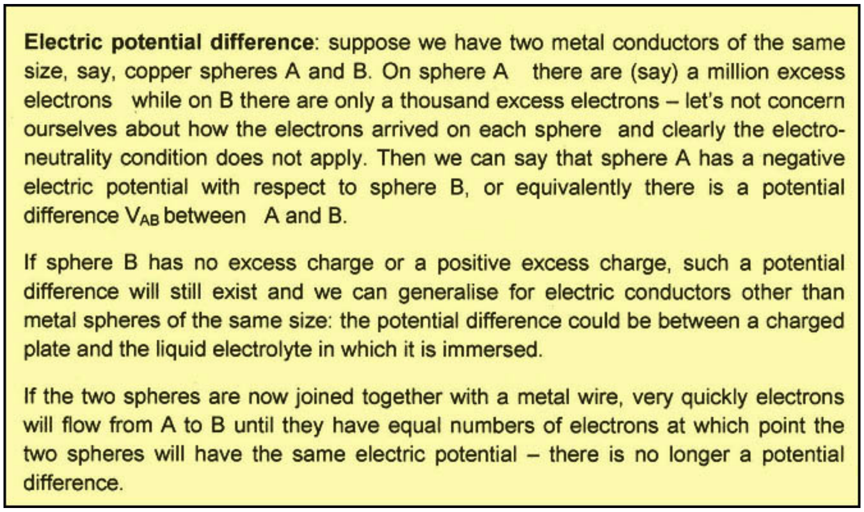
Test print showing different depths of natural "electro-tint" obtained by masking out copper plate with nail varnish; electro-etch with copper sulphate

However, at the instant of placing the plate in the solution, at the surface of the zinc some zinc atoms discard their outer electrons and move into the solution. Electro-neutrality no longer exists at the plate/solution interface: there is now an excess of Zn ++ ions in the solution adjacent to the plate (originally there are equal numbers of Zn++ and $(SO_4)^{--}$ ions in the electrolyte) and an excess of electrons (negative charge) on the plate. Very quickly, this imbalance causes a flow of Zn ++ ions back to the plate to match the flow away from the plate. In this dynamic equilibrium there is no further net loss of zinc from the plate and the resultant total current is zero.

Overall, there is a negligible loss of weight in the zinc plate but there is a significant and permanent change: an excess of electrons on the plate surface and an excess of positive zinc ions in the electrolyte very close to the metal - at the metal/electrolyte interface - remain. These surfaces of equal and opposite charge form a "double layer". The bulk of the electrolyte maintains electro-neutrality but the excess charge due to the double layer gives the metal surface a negative electric potential with respect to bulk of the electrolyte; the potential difference is around 0.5 volts.

6.2 A copper plate in copper sulphate solution

For an equivalent copper half-cell, the effect is essentially the same as for the zinc plate: a dynamic equilibrium is rapidly attained and a double layer due to excess charges is set up. In the case of copper, the equilibrium condition corresponds to a negligible mass of Cu++ ions from the electrolyte sticking on the metal surface to give it a positive electric potential with respect to the bulk electrolyte; the potential difference is again around 0.5 volts.



Electric potential difference: suppose we have two metal conductors of the same size, say, copper spheres A and B. On sphere A there are (say) a million excess electrons while on B there are only a thousand excess electrons – let's not concern ourselves about how the electrons arrived on each sphere and clearly the electro-neutrality condition does not apply. Then we can say that sphere A has a negative electric potential with respect to sphere B, or equivalently there is a potential difference V_{AB} between A and B.

If sphere B has no excess charge or a positive excess charge, such a potential difference will still exist and we can generalise for electric conductors other than metal spheres of the same size: the potential difference could be between a charged plate and the liquid electrolyte in which it is immersed.

If the two spheres are now joined together with a metal wire, very quickly electrons will flow from A to B until they have equal numbers of electrons at which point the two spheres will have the same electric potential – there is no longer a potential difference.

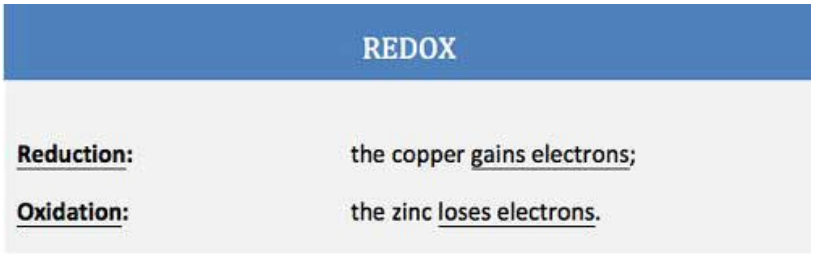
7. The basis of the saline sulphate/Bordeaux etch - mixing it up

7.1 Zinc plate in copper sulphate solution – displacement reaction

When a zinc plate is placed in copper sulphate solution something definitely happens! Spontaneously, zinc atoms at the metal surface leave electrons on the plate and move into solution as Zn++ ions; simultaneously copper Cu++ ions are attracted to the plate. The zinc ions "displace" the copper ions and this time there is no charge imbalance in the solution or at the metal surface so the reaction can carry on.

The deep colour blue of the copper sulphate solution will gradually fade (zinc sulphate is colourless); the zinc is eaten away and a layer of copper forms on the zinc plate – the copper is "plated out". With this reaction heat is produced and in practice some hydrogen gas may be produced from a side reaction involving the water.

This reaction is a spontaneous "reduction – oxidation reaction" (Redox):



REDOX	
Reduction:	the copper gains electrons;
Oxidation:	the zinc loses electrons.

Classical thermodynamics can predict the outcome of such reactions but not the dynamics of the reaction - how fast it happens - which in detail may be very complicated.
The reaction may be recognised as the basis for the widely used saline sulphate/Bordeaux etching processes (see *etchzincsteelaluminum* and *perfect chemistry*) by Friedhard Kiekeben on this website and "Bordeaux etch" by Cedric Green on his website, (*http://www.greenart.info/galvetch/bordeaux.htm*). In practice, particularly for aluminium, there may be an oxide coating on the metal plate which can effectively seal the surface. If sodium chloride is added to the solution, the chloride ions can break up this oxide surface. Due to the spontaneous nature of the reaction, chemistry rather than the etcher is in control.

8. The voltaic cell

8.1 The classic Daniell voltaic cell-taking the heat out of displacement reactions.

Test print: tone obtained with conventional aqua-tint; electro-etch, copper plate, copper sulphate electrolyte; masking out with candle wax

Although the displacement reaction just described provides a useful etching technique, for others purposes it is wasteful because the energy liberated during the process only heats the electrolyte. Far better would be to use this energy to push electrons through an external electric circuit to do useful work like driving an electric motor. Such a device, a voltaic cell, can be made by combining the zinc and copper half-cells – a Daniell cell, see figure 3 below. In effect the redox reaction is split into its reduction and oxidation reactions with each one now taking place in separate containers which are connected electrically by a salt bridge. The energy generated in the reactions is manifested as electrical energy not heat.

To describe the action, suppose that a small “pea” light bulb and switch are connected electrically between the two plates and the electrolytes in the half-cells are joined by a salt bridge. With such a “completed” circuit, when the switch is closed a current flows lighting up the bulb.

There is no further build-up of excess charge beyond that required for the original equilibrium condition for each half-cell and so the dissolution of the zinc plate continues unimpeded. Simultaneously, in the copper half-cell the concentration of the copper sulphate solution gradually reduces as copper ions from the solution stick on the plate, acquire the excess electrons which have flowed from the zinc plate and then “plate out” as a film of copper atoms. An electric potential difference is maintained between the plates; this can be measured under conditions of virtually zero electric current - the spontaneous dynamic equilibrium condition discussed earlier – with a high resistance voltmeter.

As the zinc plate is progressively consumed and the copper sulphate solution weakens, the potential difference decreases and eventually the cell stops working. The possible combinations of metals which can be used in voltaic cells and the “passive” etching described below may be determined from the so-called electro-chemical series, see section 11.3.

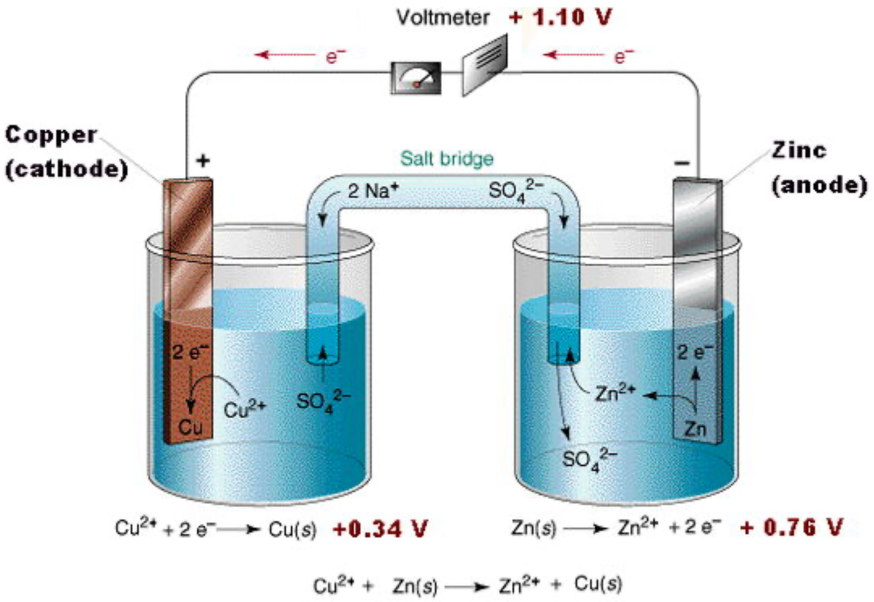


Figure 3: An example of a Daniell cell, from the Chem1 Virtual textbook
by Stephen Lower http://www.chem1.com/acad/webtext/virtualtextbook.html

Modern batteries use solid rather than liquid electrolytes and consist of multiple cells to improve the current and voltage characteristics. The term" battery" was introduced by Benjamin Franklin, by analogy with a battery of cannons, to describe cells connected together.

In general when a battery is connected to an electrical circuit:

+ terminal	accepts electrons from the circuit
− terminal	pumps electrons into the circuit

For safety, the terminals of a battery should not be connected together by just a wire, "shorted": a large current may flow in the wire causing it to get very hot.

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9. From voltaic cell to passive electro-etching.

The inherent mechanism of the classic voltaic cell - dissolving of the zinc - can be used to advantage to etch the zinc plate – passive etching - with some degree of control: the switch can be used to stop and restart the etching process. However the arrangement described above is not very practicable as it requires three electrolytes.

Test print: creating tone with cross hatching; electro-etch, copper plate, copper sulphate electrolyte; candle wax ground; after Cartier-Bresson

A simpler system for etching a zinc plate where the zinc and copper plates are placed in a single electrolyte of copper sulphate and the plates are joined together by a wire has been described by Cedric Green (see website) and Alfonso Crujera, who also included a sodium chloride reservoir add-on – see the forthcoming English edition of his electro-etching book. This would appear to be a hybrid of the basic displacement reaction in a single container and the passive electro-etching.
The characteristics of this etching technique are discussed by Cedric Green and Alfonso Crujera who has obtained comparatively short biting times when using the additional salt reservoir.

The major disadvantage of this technique and the saline sulphate/Bordeaux etching is that the copper sulphate electrolyte becomes gradually exhausted so etching times will change and at some point the solution must be replaced.
With one further step it is possible to obtain an etching process which is both controllable and does not exhaust the electrolyte which can be used for years without replacement –active electro-etching.

10. Active electro-etching: the electrolytic cell

10.1 Taking control: using a power supply to drive an electrolytic cell

10.1.1 Pumping water

The analogy of a water reservoir on a hill feeding a tank at the bottom of the hill provides a convenient way of introducing the principle of “active electro-etching”. Imagine that the water reservoir represents the zinc plate, the tank represents the copper plate, the pipe between them is equivalent to the connecting wire and the flow of water is the electron current. The water-flow is due to the gravitational potential difference –the height of the reservoir above the tank – while the electron flow is due to the electric potential difference obtained by using two different metals. In both cases, the flow rate gets larger as the potential difference is increased.

If an in-line water pump is added, the water flow downhill can be increased or the flow can be reversed and water pumped uphill. The flow of water is now determined mainly by the pump rather than the height of the reservoir above the tank and the flow rate can be changed by altering the pump settings.

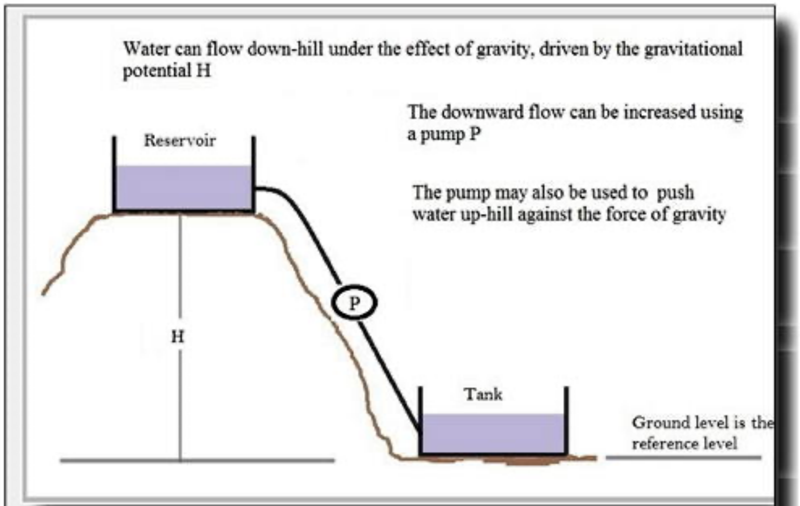

Figure 4: Pumping water – an analogy for electro-etching cells

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10.1.2 Pumping electrons

Similarly for the electrical system, an “electron pump” can be used to increase the electron flow or even reverse it and the need for dissimilar metal plates to provide a potential difference is not necessary. The “electron pump” is of course a battery or direct current power supply and the pumping capacity is determine by the battery’s voltage –the potential difference between the positive and negative terminals. For etching purposes, 0.5 -2 volts are generally sufficient but the current requirement may range from several tens of milli-amperes to tens of amperes for large plates. Larger voltages may introduce unwanted reactions, see later.

Copper test plate; electro-etch, copper sulphate electrolyte, ground: candle wax; after Talbot-Kelly

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10.2 An electrolytic cell

10.2 An electrolytic cell

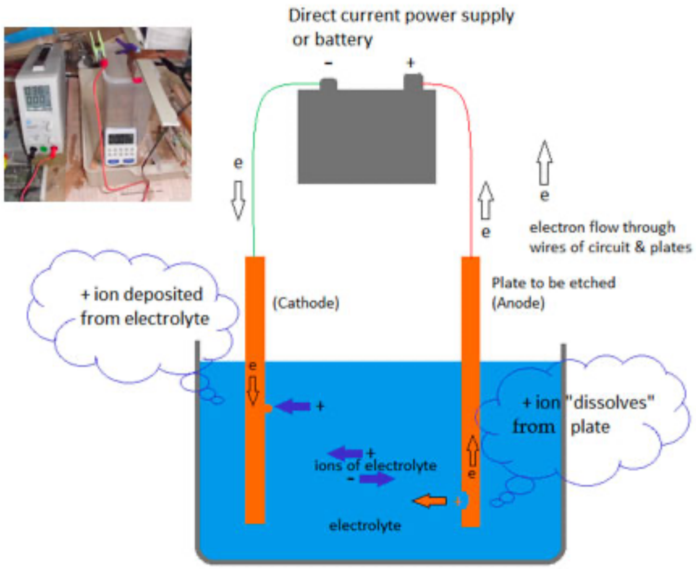


Figure 5: Schematic of an electrolytic cell: the plate to be etched is the anode, connected to the + terminal of the power supply.

A basic cell - an electrolytic cell – for, say, copper consists of two copper plates in a single container holding a copper sulphate solution electrolyte. The plate which is etched - the anode - gives up electrons to the positive terminal of the battery while at the negative terminal of the battery an equal number of electrons are pumped to the other plate – the cathode.

The process, known as electrolysis, is for us 'active electro-etching'.

When the power supply is turned on the electro-chemical process for an atom of copper is:

At the anode: a Cu atom gives up two electrons to the external circuit and dissolves in the adjacent electrolyte as a copper ion Cu++;

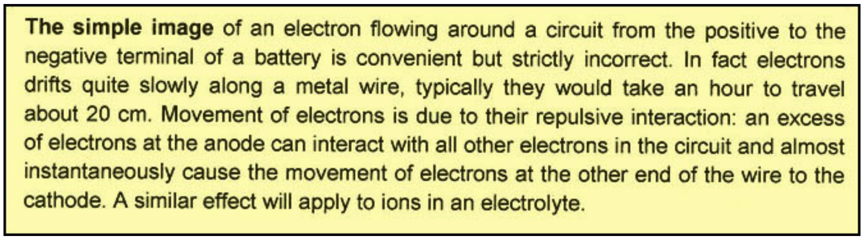
At the cathode: the cathode receives two electrons from the anode via the battery; a Cu++ ion attached to the plate accepts the two electrons and the copper atoms produced adhere to the plate – they plate out onto the electrode;

In the electrolyte (Cu++ ions and sulphate ions $(SO_4) - -$): it gains a Cu++ ion from the dissolving copper anode and loses a copper ion Cu++ to the cathode – overall the electrolyte stays electro-neutral with no loss of copper or sulphate ions.

The dissolution (dissolving) of the copper atoms provides the basis for the etching process, now driven by an external power supply.

Similar cells may be used for etching zinc and iron/steel plates using zinc sulphate and iron sulphate solutions as electrolytes. Again, provided the voltage is kept to below 2-3 volts the electrolyte remains unchanged.

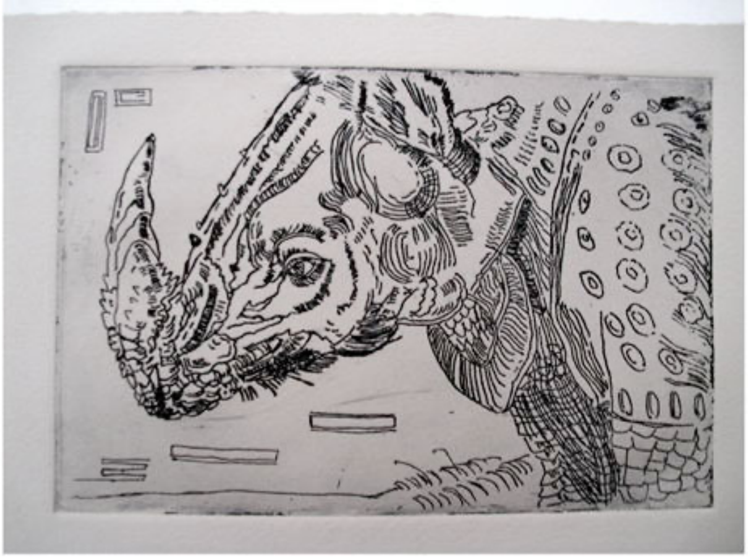
Aluminium plates immersed in an aluminium sulphate solution would not behave in a similar manner because the aluminium in solution cannot plate out onto the cathode.



The simple image of an electron flowing around a circuit from the positive to the negative terminal of a battery is convenient but strictly incorrect. In fact electrons drifts quite slowly along a metal wire, typically they would take an hour to travel about 20 cm. Movement of electrons is due to their repulsive interaction: an excess of electrons at the anode can interact with all other electrons in the circuit and almost instantaneously cause the movement of electrons at the other end of the wire to the cathode. A similar effect will apply to ions in an electrolyte.

PART 3 ELECTRO-ETCHING – GOING A LITTLE FURTHER

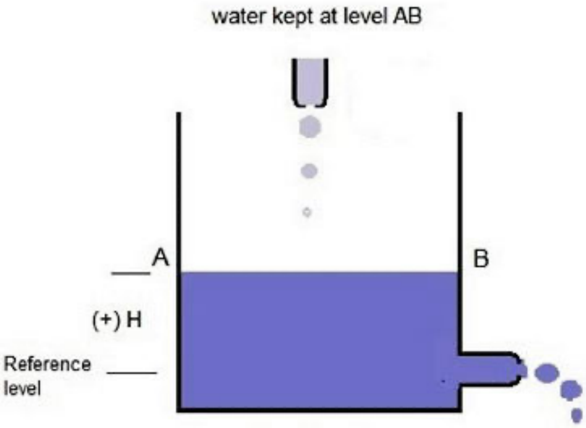
So far we have considered active electro-etching of metals at low voltages with an electrolyte made from a salt of the same metal. The process involved dissolution (etching) of the anode plate and deposition of metal on the cathode plate. By using sodium chloride solution as an electrolyte, aluminium as well as the other metals can be etched. However, the process becomes a little more complex as now it is possible for gases - hydrogen, oxygen and chlorine - to be produced at the electrodes.



After Dürer

To understand what is likely to happen, so called electro-chemical “standard potential tables” can be used. For rather trivial reasons, these tables can be rather confusing. Fortunately by using the earlier analogy of water flowing between tanks we can introduce the concepts needed, clarify the use of the standard potential tables and introduce the electro-chemical series for voltaic cells mentioned earlier. Like all analogies, it has its limitations and some terms are used rather loosely.

11. Flowing water again



Measuring the flow for different levels AB : different values of the height H, the gravitational potential

Figure 6: Spontaneous flow of water from a tank

11.1 Spontaneous reactions.

The flow of water from a hole at the bottom of a tank containing water kept at a constant level AB is shown schematically in figure 6. The flow is “spontaneous”: we do not need to do anything, gravity does it. The flow of water is driven by the gravitational potential, equal to the height H as measured from the reference position shown. The larger the height H, the greater is the flow of water out of the hole at the bottom.

Let’s call this downwards flow of water a “reaction”: it represents a real reaction which may take place in an electro-chemical half-cell, in this case the oxidation reaction for etching of a plate.

11.2 Standard potential

The height “H”, the gravitational potential difference between the surface of the water and the reference level is a characteristic of the reaction: each reaction will have a different value of H. **We will call this the standard potential for the reaction** and place a + sign in brackets in front of it. **The (+) simply means that the reaction is spontaneous.**

For **the electro-chemical equivalent of the standard potential**, the reference “ level” is now a standard reference half-cell and the standard potential is numerically equal to the electric potential difference between the electrode in the half cell with the reaction of interest and the electrode in a standard half-cell. Such standard cells are only used for this purpose. In practice the voltaic or electrolytic cells will consist of two half cells with different reactions. Significantly and usefully, the standard potential for the overall cell may be obtained from the individual standard potentials. These details need not concern us but are mentioned for completeness.

11.3 Electro-chemical series

Imagine two tanks both containing water at levels H1 and H2 respectively. Water can flow spontaneously from the higher tank, larger standard potential H1 (say), to the tank below. If the water represents the flow of electrons from one plate in a half-cell through the external circuit to a plate in a second half-cell, we can see that the higher plate must be the anode and the lower one the cathode. We have passive etching of an anode or equivalently “sacrificial corrosion”.

Potassium	K	
Sodium	Na	
Aluminium	Al	
Zinc	Zn	
Iron	Fe	
Nickel	Ni	
Tin	Sn	
Hydrogen (not a metal)	H	(reference level)
Copper	Cu	
Silver	Ag	
Platinum	Pt	
Gold	Au	

Electro - chemical series for metals

By making a table for the heights (standard potentials) H of the various half cells, with the cell with the largest standard potential at the top and the one with the smallest standard potential at the bottom – the electro-chemical series for metals - we have a means of deciding, for any pair of cells or plates, which plate is the anode (the plate etched): the one higher up in the table.

11.4 Non-spontaneous reactions

The opposite or “reverse” reaction to water flowing downwards would be water flowing upwards from the reference level to a height H. Such a reaction would be non-spontaneous: water does not flow uphill without some assistance. This reverse reaction would be characterised by a standard potential (-) H. The (-) simply means the reaction is non-spontaneous: some energy, equivalent to the potential H, must be supplied in some way to push the water upwards a height H. The larger the value H, the more non-spontaneous is the reaction and the greater the energy which must be supplied.

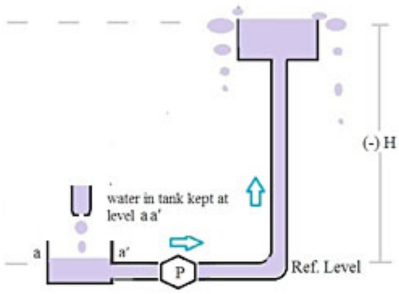


Figure 7: Non-spontaneous flow of water to a tank using a pump

11.5 Characteristics of a non-spontaneous reaction

Since our interest is in active electro-etching, we will look at pumping water up to a tank at a height H above the reference tank, to examine the features of a non-spontaneous "reaction", shown schematically in figure 7. To raise water against gravity through a potential H so that the water flows over the top of the tank requires the pump P to have a pumping energy or "pumping potential" just greater than the gravitational potential H. The difference between the pump's potential and the standard potential H is termed the "over-potential". The larger the over-potential, the greater is the flow of water.

11.6 Electro-chemical overpotential

For electro-chemical cells it is often found that an overpotential of only 0.2 - 0.4 volts above the standard potential is sufficient to produce significant electron current flow. The relation between the voltage overpotential and the electron current flow is given by the 'Butler-Volmer' equation. Sometimes, however, the overpotential at which the electric current is first seen may be well above the value expected based on the standard potential - still less than a volt but large in electro-chemical terms. This is particularly true for reactions involving the generation of oxygen and hydrogen at the electrodes for reasons which we need not discuss.

Test print: texture obtained by pushing fabric into the candle wax ground;
electro-etching, copper plate

11.7 The possibility of more than one non-spontaneous reaction occurring

Suppose two tanks at different heights, H1 and H2, with H2 larger than H1, are supplied with water by dividing the output from the pump. As the pumping potential is increased from zero, the tank at the lower height (smaller potential H1) will receive water once the pumping potential is greater than H1. As the pumping potential increases further so the over-potential for this tank gets larger, this increases the water flow to it. Only when the pumping potential is greater than H2 does water flow to the higher tank (larger potential H2).

The reaction which is the least non-spontaneous occurs first and although both reactions may be possible when the pumping potential is large enough, it is this reaction which is more active - that has a larger flow of water. The same principle holds for a larger number of tanks/non spontaneous reactions.

It will be seen for electro-etching that by comparing the standard potentials for different reactions, some idea can be obtained as to which reactions will occur at the anode and cathode electrodes.

11.8 Spontaneous and non-spontaneous reactions occurring together

Using the analogy of the last section, a spontaneous reaction can be thought of as one for which the height of the tank above the reference level is zero. Consequently, for all pumping potentials greater than zero, the pump will increase the flow of water for this spontaneous reaction while for the non-spontaneous reactions nothing will happen until the critical heights (standard potentials) are exceeded.

12. From water pumping to electro-etching reactions

As discussed previously, the water pump is analogous to a battery or direct current power supply. The tanks represent half-cells in which various reactions take place. The flow of water between tanks represents the flow of electrons between electrodes through the outer circuit - the connecting wires. The water flow analogy does not consider any aspects of the electrolyte.

The equivalent of the gravitational standard potential for a tank, the height H, is now the standard potential for a specific electro-chemical reaction in a half cell. We can treat the values of the electro-chemical standard potential in a similar way as we did for the gravitational analogy: (+) and (-) denote spontaneous and non-spontaneous reactions respectively.

12.1 Some electro-chemical reactions - etching plates

Let's look again at some reactions related to electro-etching. For example the electro-etching of zinc is given by the oxidation reaction:

after Michelangelo

$Zn(s) \rightarrow$ $Zn(aq)^{++} + 2e^{-}$ (+) 0.76 V Standard potential

The zinc plate which is the anode gives up electrons to the external circuit and zinc ions 'dissolve' into the electrolyte. The (+) signifies that the reaction is spontaneous. This reaction is one of the half-cell reactions in the Daniel cell.

The reverse, reduction reaction is:

$Zn(aq)^{++} + 2e^{-}$ $\rightarrow Zn(s)$ (-) 0.76 V Standard potential

This reaction is non-spontaneous - the (-) sign. In this case, zinc from an electrolyte, say, of zinc sulphate would be deposited on the cathode plate. To obtain the reaction it would be necessary to make the cathode part of an electrochemical cell driven by a power

supply.
Similar oxidation reactions apply for electro-etching aluminium and iron. They are spontaneous with standard potentials of (+) 1.66 V and (+) 0.44 V respectively. Copper does not follow this trend, its reduction reaction (depositing copper on a cathode), not its oxidation, etching reaction, is spontaneous with a standard potential of (+) 0.34 V. Hence passive etching of copper is only possible if the other electrode is silver, platinum or gold (see the electro-chemical series and standard potential tables).

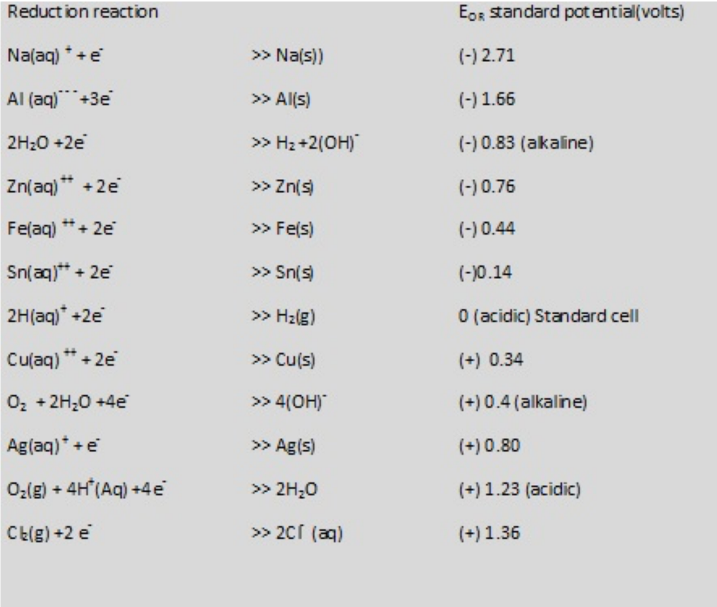
Stencil made by electro-etching through thin sheets of coated aluminium; sodium carbonate electrolyte

12.2 Standard potential tables

The example for zinc above shows that it is not necessary to write down both the oxidation and reduction reaction equations. If one reaction is known the reverse reaction is obtained from it by reversing the arrow in the equation and changing the sign in front of the standard potential.
Tables of standard potentials have been prepared for a wide range of possible electro-chemical reactions. By convention, they give the chemical equation and the (+) or (-) sign for the reduction reaction alone. A small selection is shown in the table below. These values apply when the concentration of the solutions of the ions or molecules is 1 mole per litre (1M).

Practical concentrations may often be different so consequently conclusions based on the standard potentials should only be taken as indicative. The actual potential in these circumstances can be found from the standard potentials by using the Nernst equation.

Understanding the details of the electro-chemical equations shown is not critical, it is sufficient to appreciate the significance of the (+) or (-) sign and the relative values of the standard potentials for different reactions.



Reduction reaction		E_{OR} standard potential(volts)
$Na(aq)^{+} + e^{-}$	>> Na(s))	(-) 2.71
$Al\ (aq)^{---} + 3e^{-}$	>> Al(s)	(-) 1.66
$2H_2O + 2e^{-}$	>> $H_2 + 2(OH)^{-}$	(-) 0.83 (alkaline)
$Zn(aq)^{++} + 2e^{-}$	>> Zn(s)	(-) 0.76
$Fe(aq)^{++} + 2e^{-}$	>> Fe(s)	(-) 0.44
$Sn(aq)^{++} + 2e^{-}$	>> Sn(s)	(-)0.14
$2H(aq)^{+} + 2e^{-}$	>> $H_2(g)$	0 (acidic) Standard cell
$Cu(aq)^{++} + 2e^{-}$	>> Cu(s)	(+) 0.34
$O_2 + 2H_2O + 4e^{-}$	>> $4(OH)^{-}$	(+) 0.4 (alkaline)
$Ag(aq)^{+} + e^{-}$	>> Ag(s)	(+) 0.80
$O_2(g) + 4H^{+}(Aq) + 4e^{-}$	>> $2H_2O$	(+) 1.23 (acidic)
$Cl_2(g) + 2e^{-}$	>> $2Cl^{-}$ (aq)	(+) 1.36

Standard reduction potentials in water solutions at 25°C; concentration of solutions 1 mole per litre (1M).

12.3 Spontaneous and non-spontaneous reactions occurring together

The spontaneous electro-etching reactions of zinc, aluminium and iron can in principle take place by passive etching in a voltaic cell using appropriate electrolytes and the correct combination of plates as obtained from the electro-chemical series.

Alternatively, the plate to be etched can be made the anode plate in an electrolytic cell driven by a power supply - active electro-etching. Then, the action of the power supply is to increase the rate of these spontaneous reactions: it speeds up the etching.

The use of a power supply means that it is also possible for non-spontaneous reactions to take place if the applied voltage is larger than the required standard potential for the reaction(s). If both spontaneous and non-spontaneous reactions are possible at an electrode, the spontaneous reaction will be the preferred or dominant reaction with the non-spontaneous reaction possibly occurring as a secondary reaction, see sections 11.7 and 11.8.

Copper plate after electro-etching in sodium chloride electrolyte

12.4 Gaseous electro-chemical reactions at electrodes

Of interest are the reactions involving the evolution of gases at the cathode or anode of a driven electrolytic cell.

<u>At the anode:</u>

Evolution of chlorine:

$$2Cl^- (aq) \rightarrow Cl_2(g) + 2e^- \qquad (-)1.36\ V$$

Chlorine ions in the electrolyte give up electrons to the anode plate/external circuit and the chlorine atoms combine to form chlorine gas. The oxidation reaction is non-spontaneous.

Evolution of oxygen:

$$2H_2O \rightarrow O_2(g) + 4H^+(Aq) + 4e^- \qquad (-)\ 1.23\ V\ (acidic)$$

The reaction is non - spontaneous and comparing the value of its standard potential with that for chlorine it should be the preferred reaction. However, the rate of reaction is relatively slow and at high concentrations of chlorine ions, chlorine not oxygen is liberated.

Because H+ ions are produced at the electrode there is an excess of them and around the electrode the electrolyte solution is acidic, see section 13.

<u>At the cathode:</u>

Evolution of hydrogen:

$2H_2O + 2e^- \rightarrow H_2 + 2(OH)^-$ (-) 0.83 V (alkaline)

The reaction is alkaline because as the hydrogen is liberated at the cathode there is an excess of (OH) − ions so that locally the solution becomes alkaline, see section 13.

12.5 Why copper, zinc and iron can be deposited onto a cathode

The standard potentials for deposition of copper, zinc and iron - a reduction reaction at the cathode - are (+) 0.34 V, (-) 0.76 V and (-) 0.44V respectively. The relevant standard potential for the generation of hydrogen is (-) 0.83 V and for evolution at a zinc cathode there is an additional over-potential before a current is seen of around 0.4 V (total (-) 1.23 V). Consequently the hydrogen reaction is more non-spontaneous than the reactions for the deposition of these three metals onto a cathode from an electrolyte containing their ions.

12.6 Why sodium and aluminium cannot be deposited onto a cathode

In contrast to the deposition of copper, zinc and iron, the reason that sodium and aluminium cannot be deposited onto the cathode of a driven cell from their ions in solution is because their standard potentials, (-) 2.71 V and (-) 1.66 V respectively, show that they are much more non-spontaneous than the generation of hydrogen, (-) 0.83 V, which is the preferred reaction.

12.7 Variation of current with voltage -passivity

The explanation of the electrolytic cell would suggest that as the applied voltage is increased so the current flowing through the cell and the rest of the circuit should increase. Sometimes it is possible to observe that the current remains constant or even decreases as the voltage is increased –a so-called passive region. The reasons for such behaviour are beyond the scope of this article but may be related to the inability of ions to reach the electrodes fast enough, the blocking of the electrode surface to ions due to the gases produced and the complexity of the reactions taking place.
Generally it should possible to find a current/voltage region with characteristics that allow etching at suitable currents. We mention the present effect for those rare occasions when you may find strange things happening during etching: it probably is not your fault!

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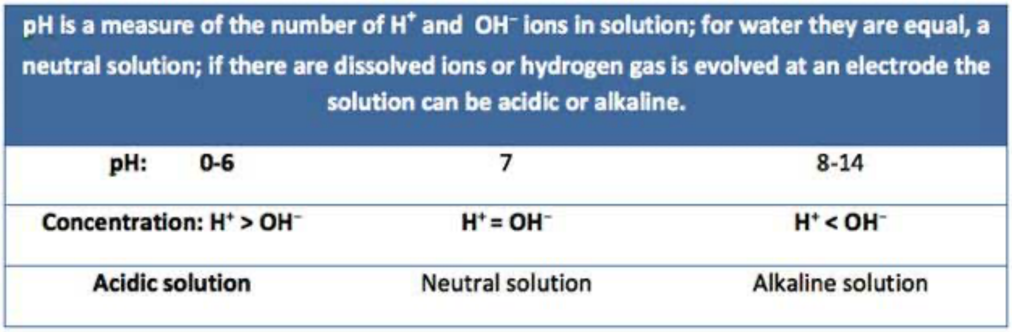
13. The use of common salt, sodium chloride, as an electrolyte

Common salt dissolved in water has been used as an electrolyte to carry out electro-etching. It is cheap, easy to handle and can be used to etch copper, zinc, aluminium and mild steel (iron). Compared to the metal/same metal sulphate electrolyte combinations considered earlier it introduces some additional effects.



pH is a measure of the number of H^+ and OH^- ions in solution; for water they are equal, a neutral solution; if there are dissolved ions or hydrogen gas is evolved at an electrode the solution can be acidic or alkaline.

pH: 0-6	**7**	**8-14**
Concentration: $H^+ > OH^-$	**$H^+ = OH^-$**	**$H^+ < OH^-$**
Acidic solution	Neutral solution	Alkaline solution

Sodium chloride readily ionises to form Na+ and Cl− ions while water, although a very poor electrical conductor, ionises one molecule in every ten million, splitting into a positive hydrogen ion H+ and a negative hydroxyl ion OH−. At the cathode of the cell the preferred primary reaction is the evolution of hydrogen over the deposition of sodium since the latter is a more non-spontaneous reaction.

At the anode both the chlorine ion and the hydroxyl ion could give up their electrons and evolve as chlorine or oxygen gases respectively. For an inert platinum anode these gases can indeed be seen: chlorine is produced at high salt concentrations, oxygen at low and both at intermediate values. However when etching, these non-spontaneous reactions must compete with the dissolution of the metal anode - aluminium, iron and zinc metal plates (spontaneous reactions) and copper (less non-spontaneous than the gaseous reactions).

Yellow cuprous oxide produced in sodium chloride electrolyte after electro-etching a copper plate

Consequently, dissolution of the metal anodes rather than evolution of chlorine or oxygen is the preferred reaction. Secondary reactions can occur between the dissolving metallic ions and the ions in the electrolyte to produce metallic oxides, hydroxides and chlorides. Should excessive voltages be used, then chlorine or oxygen gases may be given off at the anode so such a possibility must at least be considered when designing etching equipment using sodium chloride electrolyte. At the cathode, say a copper plate, the evolution of hydrogen gas may be expected even at low voltages.

When electro-etching aluminium in sodium chloride solution a surprise may be obtained: a gas can be generated at the anode which is neither chlorine nor oxygen but is in fact hydrogen. A 'parasitic' chemical reaction (independent of the current) may take place between the water and the aluminium.

The conclusions drawn from the use of standard potentials should only be taken as indicative since actual experimental or etching conditions may be different. Only the basic reactions have been given, others are possible.

Zinc plate after electro- etching in sodium chloride electrolyte

Neither hydrogen nor oxygen dissolve readily in water and so bubbles of both would be seen if they are produced. At room temperatures, chlorine by comparison can be absorbed by water, around 6g/litre. Furthermore if the electrolyte is stirred the chlorine ions from the anode region can interact with the hydroxyl ions from the cathode region and sodium hydroxide solution, caustic soda, may be formed. As result, although chlorine may be produced, for a period of time it can be retained within the electrolyte solution.

Although sodium chloride electrolyte is in use in some studios, recently there have been some strong views expressed against its use. The issues involved are discussed in the appendix.

14. Amount of gas produced at an electrode.

Given that there is the possibility of generating chlorine, oxygen and particularly hydrogen which may have no competing reaction, it would be useful to have some idea of the quantities of gases which may be produced electro-chemically even if the estimate is an upper value. The reaction equations may be used to achieve this. Note, the parasitic generation of hydrogen when etching aluminium is not included in these considerations.

For hydrogen it is found that for a current of 1 ampere and an etching time of one hour, approximately 0.42 litres or 420 c.c. of gas are generated. Since the volume of gas produced is proportional to current (amperes) multiplied by etching time (hours) the amount of hydrogen produced for different currents and etching times can be found on a pro rata basis.

For the same time and current the equations indicate that the same volume of chlorine and half the volume of oxygen would be produced.

These values give an upper limit on the amount of gas that may escape from the etching cell since in each case they assume that no other reaction is taking place at the electrodes. The figures for oxygen and hydrogen correspond to those for complete electrolysis of water. The value for chlorine does not take into account that some of the chlorine produced might be absorbed by the water or react chemically with hydroxyl ions.

15. Conclusion

In this article we have presented the basic principles which underpin practical electro-etching using simple equipment and procedures. Although the real world can be more complex, generally the electrolytic cells used for electro-etching, particularly those using the same metal/metal sulphate electrolyte, are well behaved and can be adequately explained by the present simplified treatment.

The use of sodium chloride solution as an electrolyte offers in principle the possibility of electro-etching aluminium as well as copper, iron (mild steel) and zinc, although for these latter metals it provides no obvious etching advantage. At present, the use of this electrolyte is for the informed electro-etcher who wishes to explore, quantify and resolve the issues associated with its use and who is capable of doing this in a safe manner.

16. Bibliography

References are too numerous to mention individually. An exception is “The Usborne Illustrated Science” which gives accessible explanations enhanced by excellent illustrations. Most of the ground covered can be obtained from the internet; Wikipedia articles are often a good starting point. Two sites are particularly recommended:

The Physics Classroom:

http://www.physicsclassroom.com ; the subject of electricity is dealt with in a very approachable way requiring little prior knowledge.

An excellent general chemistry virtual textbook which includes electrochemistry is authored by Dr Stephen Lower: http://www.chem1.com/acad/webtext/virtualtextbook.html.

The English version of Alfonso Crujera’s handbook “ Electro-etching handbook – a safe, nontoxic approach” may be ordered from Amazon or directly online from the publishers:

http://www.readontime.com/ISBN=9788493510091

From Europe:

http://libros.elmundo.es/detalle.aspx?lang=es&isbn=9788493510091

See also: “Electro–etching Made Easy” under

➡ etching innovation on this website.

APPENDIX: PRACTICAL SAFETY ISSUES RELATED TO USING SODIUM CHLORIDE ELECTROLYTES FOR ELECTRO-ETCHING

It was not the original intention of this article to deal with practical issues -these are covered in the electro-etching handbook. However, due to the characteristics of sodium chloride (brine) electrolytes and their possible implications for safe electro-etching it is necessary to include some comment.

The use of sodium chloride electrolytes has been promoted in the book 'Print-making Revolution - new advancements in technology, safety, and sustainability' by Dwight Pogue, Watson-Guptill (2012), and for a number of years has been incorporated in the electro-etching practices at the University of Costa Rica, see 'Five years of total abstinence of any acid: University of Costa Rica's School of Fine Arts Non-Toxic printmaking experience.' by Francisco Hernandez-Chavarria and Alberto Murillo, Arte, Individuo y Sociedad, 2012, 24(2) 167 - 177. These activities have been undertaken within reputable art schools, presumably without apparent mishap.

Recently Cedric Green, an eminent galv-etcher, on his website, www.greenart.info, has warned against the use of sodium chloride electrolytes, citing websites related to the chlor-alkali industry and several material safety data sheets (MSDS) but with little explicit explanation (website as accessed on 10/1/14). In common with all activities involving chemicals, electro-etching should not be undertaken without a careful assessment of the risks and the safety precautions required and so the fact that Cedric Green raises concerns should be taken seriously. Some perspective is required.

To be clear, a chlorine ion (Cl-) in a solution of water, as obtained when dissolving common salt in a beaker of water, for our purposes is not a hazard. It is what happens to the chlorine ions when they are subjected to electrolysis which is at issue. The article "Brine Electrolysis", www.electrochem.cwru.edu/encyc/art-b01-brine.htm, provides a succinct and helpful review of industrial brine electrolysis -the chlor-alkali industry.

Industrially, the electrolysis of sodium chloride solutions is used to produce chlorine gas, hydrogen gas, sodium hydroxide solution (commonly called caustic soda) and additionally, by combining the chlorine gas and sodium hydroxide, sodium chlorate or sodium hypochlorite (commonly known as bleach or hypo) can be made. What is actually obtained from the electro-chemistry depends on the design of the plant and the operating conditions. For example, a high concentration of sodium chloride solution (100's g/litre) is required for making chlorine gas and sodium chlorate which also needs an acidic solution and processing temperatures around 60 degrees Celsius, whereas for sodium hypochlorite production a weaker, alkaline sodium chloride solution (10 g/litre) is used.

All of the above chemicals, depending on their concentration, are hazardous. Remember, however, that caustic soda and bleach, at relatively low concentrations, are used safely in the home, but they can still be hazardous if miss-used and there are requirements concerning their disposal.

As seen in earlier sections, in electro-etching, hydrogen and caustic soda, at low concentrations, will certainly be produced when using sodium chloride electrolyte and must be dealt with appropriately. The concern lies more with the consequences of the possible formation of, chlorine gas and its release from the electrolyte solution, and sodium chlorate. Independently, with the use of the sodium chloride, the metallic ions etched from the anode can chemically interact with the solution to give by-products which may pose issues for handling and environmentally safe disposal, for example, copper compounds arising from etching copper plates.

A distinction, apart from the scale, must be made between industrial electrolysis operations and electro-etching:

- industrially, large quantities of product, at relatively high concentrations are made as efficiently as possible; this requires the use of ***inert electrodes made from materials which suffer minimal corrosion;***
- For electro-etching the aim is to ***cause as much corrosion-etching - of the anode electrode as possible*** with minimum formation of by-products, at low concentrations, in an inefficient way.

From the electro-chemistry we have seen that for active electro-etching using a power supply, the etching of the anode plate is a more spontaneous reaction than the forming of either chlorine molecules from chlorine ions or oxygen from the water and consequently is the ***'preferred reaction'*** - the one most likely to take place, at the fastest rate.

In essence, the concerns about unwanted chemical products resulting from the chlorine reduce to this question: ***to what extent is the etching of the anode the preferred reaction as compared to the formation of chlorine at the anode, and how much does***

this change the characteristics of the electrolysis process as compared to using an inert metal anode?

To aid the discussion several possibilities can be envisaged. As a reference point for illustration, the products obtained from the electrolysis of a brine solution, volume 1 litre, initial sodium chloride concentration 50g/litre (say), for one hour with an electric current of 1 or 10 amperes(A), at room temperature, with *ideal inert electrodes* and 100% efficiency of operation, will be considered. The quantities of the products produced by the passage of the electric current may be found from standard equations, see 'Brine Electrolysis'.

A.) Etching of the anode plate dominates so that the formation of chlorine or oxygen and their effects are negligible.

This is the ideal situation. However, hydrogen is still produced at the cathode, ≈ 0.4 litres (1 A); ≈ 4 litres (10 A), together with sodium hydroxide, upper limits ≈ 1.5g (1A); ≈ 15g (10A). Adequate ventilation is required: sufficient air movement to disperse the hydrogen into the outside atmosphere with equipment well away from flames or any sources of ignition -a risk assessment should be made.

The concentrations of sodium hydroxide, assuming it is well mixed in the electrolyte are small - at most 0.15 and 1.5% by weight, but there will be an accumulative effect with repeated etchings. Of more importance may be the by-products formed from the chemical reactions of the metal ions and the electrolyte - often hydroxides, oxides or chlorides of the metal. Again, the products may be present in small quantities and not pose a personal safety issue, provided good laboratory/studio safety practice is observed, but they may still require appropriate disposal to comply with environmental legislation.

In attempting to assess what by-products may occur and their consequences it is important to remember that they will be present in aqueous rather than solid form and in concentrations usually far less than those quoted in MSDS sheets. Some useful guidance in a readable form -'Student Safety Sheets' and 'Hazcards' - can be found from the UK website of CLEAPSS®: www.cleapss.org.uk. Generally, the range of chemicals which can be disposed of via the studio/laboratory sink/sewer waste system is quite restrictive and typically concentrations must be no more than one percent and quantities not more than a few litres per day without approval (information taken from 'Guide to Laboratory Sink/Sewer Disposal of Wastes, Vanderbilt Environmental Health and Safety, Vanderbilt University, USA; www.safety.vanderbilt.edu).

B.) The formation of chlorine molecules and their escape from the anode in gaseous form, predominates the process.

This represents the other extreme to (A). Apart from representing a very ineffective etching system it would be unacceptable from a safety standpoint. The quantities of chlorine evolved in an hour are: ≈ 0.4 litres (1 A) and ≈ 4 litres (10A). This is an unrealistic situation which if it were to arise would indicate that there was something wrong with the etching set-up. However it allows us to mention some related points applicable to other situations.

Gaseous emissions from the anode may be incompatible with the hydrogen from the cathode: hydrogen and chlorine mixing in strong sunlight can explode as can oxygen and hydrogen mixed in the presence of a source of ignition. These are extreme cases but illustrate that it is good practice to keep gaseous emissions from the electrodes separate.

The smell from house-hold bleach or hypo is in fact the smell of low levels of chlorine. At 3 ppm (parts per million) chlorine can be detected by the nose (not that this can be relied on as a fool proof method of detection) and after an hour can cause mild mucous membrane irritation. Immediate chest pains, vomiting and coughing occur at 30 ppm while at 430 ppm chlorine is lethal after 30 minutes. For practical purposes if there is any sustained smell of chlorine around electro-etching equipment its use is highly questionable.

To strike a balance, it must be said that chlorine gas can be produced at the levels indicated and kept within the electrolyte solution to produce hypochlorite (bleach) at low concentrations. We will look at such systems next.

C) Chlorine molecules are produced by the electrochemical reaction but remain within the electrolyte.

'Electro-chlorination' systems roughly comparable with electro-etching units in terms of the current used, a few amperes, but with an inert anode electrode are available commercially to produce sodium hypochlorite (bleach) which is then used to treat water - over a billion people worldwide have inadequate drinking water. Such systems are designed to retain the chlorine molecules within the electrolyte and minimise the splitting of the sodium hypochlorite which may result in the formation of sodium chlorate, a compound of low oral toxicity. The methods to achieve this provide some useful guidelines for potential electro-etching systems:

- To ensure that there is adequate solubility for the chlorine molecules so that they remain in solution and to minimise the chemical transformation of sodium hypochlorite to chlorate, the concentration of the initial sodium chloride should be less than 50g/litre and the unit should be operated around 20 degrees Celsius, room temperature, with a slightly alkaline pH;
- To assist solubility of the chlorine molecules use as large a volume of electrolyte as practicable and not less than one litre;
- To encourage the mixing of the sodium hydroxide produced in the cathode region with the chlorine molecules Cl2 (aqueous) in solution around the anode the electrodes should not be too far apart and the electrolyte may be stirred.

Assuming no sodium chlorate formation, the amount of sodium hypochlorite produced in an hour for ***inert electrodes*** would be around 1.5g (1 A) and ≈ 15g (10A) to give concentrations of 1.5g/litre and 15g/ litre. In actual electro-chlorinators, an upper limit of around 8g/litre may be obtained due to secondary reactions at the cathode. Such concentrations ≈ 1% by weight are lower than household bleach at 5 - 10%. In practice, low levels of sodium chlorate may be present and it is necessary to ensure that when the chlorinated solution is added to drinking water the concentration of chlorates is below prescribed limits (see below).

Some useful data are contained in the report 'Development of a small-scale electro-chlorination system for rural water supplies' by David L Key et al, WRC Report No 1442/1/09 (2010) - can be downloaded from the internet. This report describes the development of a continuous flow unit to efficiently produce sodium hypochlorite on a small scale.

For what were considered optimised conditions with an inert, so-called "ROTA" anode -the best anode material used in the study - the following was found (see table 3.1 of the report):

Running conditions: sodium chloride 25g/litre; applied voltage 3.2V, current 0.4 A, current density 12mA/cm2;

Total Chlorine produced per hour: 0.37 g (at 0.4 A);

Current efficiency: 68.7 % (100% signifies all the current is used to form Cl2);

"Freely available" chlorine concentration: 7.3 g/litre

Sodium chlorate concentration: 32 mg/litre

The unit was designed to minimise the amount of sodium chlorate produced and side reactions reducing the efficiency. According to the authors, given that the output from the unit was used to dose large quantities of water, the limit for sodium chlorate in drinking water, 0.7mg/litre could easily be achieved.

Of interest for electro-etching are the corresponding results for the same operating conditions when using an anode material "DMTA" which proved unsatisfactory because it corroded:

Total Chlorine produced per hour: 0.8 mg (at 0.4 A);

Current efficiency: 2.1 % (100% signifies all the current is used to form Cl2);

'Freely available' chlorine concentration 0.2 g/litre

Sodium chlorate concentration: 1 mg/litre

It is seen for the corroding anode there is around x 30 reduction in the amount of chlorine -as shown from the efficiency- and sodium chlorate produced as compared to the best inert 'ROTA' anode. For oral toxicity estimates of the solution, the concentration of sodium chlorate is very small.

A similar trend in the reduction of chlorine generation is reported by another group when testing different anode materials in a simple, non-optimised electro-chlorinator set up for treating seawater. A significant decrease in sodium hypochlorite levels was observed when aluminium, copper and zinc anodes were used instead of an inert anode material (see M Saleem 'Biofouling Management in the Cooling Circuit of a Power Industry using Electrochemical Process'
J Chem. Soc. Pak., vol 33, no 3 , 295 -303 ,(2011) and M Saleem et al 'On site Electrochemical Production of Sodium Hypochlorite Disinfectant for a Power Plant utilizing Seawater' Int J Electrochem Sci, 7 (2012) 3929 -3938, both obtainable from the internet).

In the latter paper, a simple system was used consisting of two electrodes, each 18 x 17.5 cm, separated by 6- 8 cm, held in a cylindrical vessel with 3 litres of seawater, concentration of Cl- 24.5 g/litre and of Na+ 14.5 g/litre. Comparing an inert titanium anode with aluminium, copper, zinc and stainless steel anodes the following effective concentrations of sodium hypochlorite were obtained after an hour at a current of ≈ 20A

Material:	mg/litre sodium hypochlorite
Titanium with DSA coating	6000
Stainless steel	1010
Zinc	920
Copper	230
Aluminium	34

Using the value of 22.7A derived from an optimum current density of 72. mA/cm2 which gave around 6300mg/litre, the current efficiency for the titanium anode is ≈ 63 % and by comparison that for the aluminium is ≈ 0.4 %. In similar work using a continuous flow unit (first paper), it was claimed that the chlorates found were negligible (but no value given) and that the active chlorine was totally in the form of hypochlorite.

The above work suggests that it should be possible to make an electro-etching system that can retain any chlorine produced within the electrolyte and that in comparison to an electro-chlorinator should produce less chlorine Cl2 (aqueous) and consequently less sodium hypochlorite and sodium chlorate. There may be implications for the re-using of the electrolyte and its eventual disposal depending on the presence and concentration of any sodium hypochlorite and sodium chlorate.

While these results are encouraging they are not conclusive. The question remains: how do I know what my electro-etching system is producing? This requires similar studies for actual electro etching over a wide range of conceivable etching conditions to establish the extent and concentration to which chlorine, any associated by-products and other by products are formed. The possibility of de-chlorination, if required, using sodium thiosulphate or ascorbic acid, as used for swimming pools, and the use of cheap chlorine indicators (equivalent to litmus paper) which can detect a few mg/litre could be usefully explored.

Another question can be asked: given these uncertainties why bother with sodium chloride electrolytes? The attraction of sodium chloride, common salt, as compared to copper, zinc and ferrous sulphate (same metal salts) is its ready availability, which may be important in some countries, its ease of handling and its perceived lower cost - in the UK copper sulphate can cost ten times as much as common salt. This last point may be a false economy: the other electrolytes can be used for a long time since the etching does not alter the electrolyte significantly whereas the sodium chloride electrolyte, due to the by-products will need to be changed and disposed of in an acceptable manner.

From an etching viewpoint, it is difficult to see what advantage sodium chloride electrolyte has for electro-etching copper, zinc and iron/mild steel as compared to same metal salt electrolytes. Further, from an 'environmentally good practice' viewpoint it is better to use the electrolyte which produces less waste for disposal and less hydrogen gas - the 'same metal salt electrolyte' approach.

For aluminium, however, the situation is different since there is no equivalent to the metal/same metal salt electrolyte systems that exist for the other metals: aluminium cannot be deposited on a cathode in preference to the evolution of hydrogen gas.

Importantly, in addition to providing the conducting electrolyte which allows electric current to flow in the solution, sodium chloride provides chlorine ions which can breakdown the nanometre thick oxide layer which usual exists on the surface of aluminium - so-called 'pitting' corrosion. In contrast to inert electrodes, the interaction of the chlorine ions with the aluminium anode to achieve the disruption of this layer is more complex: initially the dissolution (etching) of the aluminium surface results in localised soluble complexes of either hydroxyl or chloride ions [$Al(OH)_2Cl$, $Al(OH)Cl_2$] which subsequently transform within the electrolyte solution to aluminium hydroxide [$Al(OH)_3$], a low hazard gelatinous precipitate. In these circumstances, whether or not the formation of sodium chlorate is significant may be questionable.

The role of sodium chloride suggests other approaches: using an electrolyte made up from two salts, one to provide the electrical conductivity combined with a minimum of sodium chloride solely to break down the oxide layer; alternatively the use of an alkaline electrolyte using sodium carbonate which can disrupt the oxide layer without the need for chlorine ions. Whether or not these approaches have their own surprises is unknown to the present authors but they would be worth investigating. Don Braisby at Glyndwr University, UK is currently looking at non-toxic methods of electro-etching aluminium.

In the English edition of the Electro-etching Handbook, the opinion, at the time of writing October 2012, was that it remained an open question as to whether or not the use of sodium chloride electrolyte was an addition to so-called 'non-toxic' methods. This is still the case in January 2014. In this appendix we have sought to present the issues as we see them, provide a balanced view and indicate what could be done to make the situation clearer. Others may have differing views. The technique using sodium chloride is not for the casual etcher but for the experienced and informed etcher who is aware of the issues, wishes to explore them and is capable of doing so in a safe way.

Note added December 2014. Recently Cedric Green has added an appendix to his website related to the issue of sodium chloride. We have carried out some electrolysis experiments using aluminium electrodes and sodium chloride solution as the electrolyte and for the conditions studied did not detect any chlorine. For more information see an updated version of our article at

www.crujera.com.,

English/publications/articles