

APPENDIX C (GREEN PRINTS)

THE CHEMISTRY OF THE ELECTROLYSIS OF SALT SOLUTION USED FOR ETCHING DIFFERENT METALS

The use of Sodium Chloride (brine or salt solution) as an electrolyte in galv-etch or any type of electro etching is often advocated, and assumed to be safe, convenient and economical. But there are complex chemical reactions involved that are not as safe as the solutions recommended for etching Copper, Zinc and steel described in Green Prints and this website. They result from the separation of the Chlorine ions and the Sodium ions in the water solution, and their reactions with the metal ions of the anode plate or in solution. There are secondary reactions between the solutions produced which result in more or less toxic and unstable precipitations. For nearly all metals there are large volumes of insoluble precipitations produced, which can block lines and prevent even etching, and require frequent filtering of the electrolyte. There is always copious production of hydrogen which is explosive and to which many people are allergic. The process of electrolysis is not reversible, in other words, metal cannot be deposited on a plate or object by making it the cathode instead of the anode. The filtered solution cannot be used indefinitely as its chemistry and concentration can change over time, and must be disposed of safely.

For a printmaker, it is inadvisable to risk the contact with these solutions and gases, to have the problem of the unpredictability of the results of using a gradually changing electrolyte and to be faced with the necessity for disposal of spent solutions. It is extremely inconvenient to have large volumes of precipitate, and to have to a high level of ventilation over the etching tank to remove the gases. Remember that, for example, using a Zinc Sulphate electrolyte with Zinc plates, or Copper Sulphate with Copper plates, results in an unchanging solution that only requires occasional filtering, reversibility, no precipitate, and no gases. I have been using the same solutions since 1991, only filtering and topping them up very occasionally. Printmakers are not chemists and cannot be expected to take the extraordinary precautions that are required in a laboratory to isolate gases or dangerous chemicals or to know when the solutions they are using are changing and becoming unusable. The principle of precaution should be applied, and only tried and tested methods should be used.

SALINE SULPHATE ETCH

The use of a mixture of salt and Copper Sulphate called "Saline Sulphate etch" is promoted as an alternative to using "Bordeaux Etch" which is pure

Copper Sulphate for etching zinc, iron, and aluminium without needing to use electricity. Note that under certain circumstances Copper Chloride (CuCl_2) and Sodium Sulphate (NaSO_4) are produced when adding salt to Copper Sulphate. Copper Chloride is a very toxic chemical. Sodium Sulphate is known as "Glaubers Salt" once used as a laxative, and it is also a Eutectic salt, whose solid melting point of between 40°C and 50°C makes it useful for storage of heat. See below for precise details of the circumstances and the proportions of NaCl and CuSO_4 that can produce the reaction.

GENERAL DESCRIPTION OF PROCESSES

The descriptions below show in detail, the processes of the electrolysis of Sodium Chloride, 'salt solution or brine), and the reactions with the Chlorine gas that occur when different metals are etched. The secondary reactions between the metal Chlorides produced and the caustic soda that is always generated whatever metal is etched, are described and illustrated. The hazards and ill effects of the chemicals that are produced is listed. Some of these reactions can be found with Saline Sulphate Etch if it is used electrolytically in the passive Galv-On process or by mistake as an electrolyte for etching copper.

Electrolysis of Sodium Chloride solution produces Chlorine gas at the anode and hydrogen gas at the cathode, leaving a solution of Sodium Hydroxide (caustic soda). If the anode (+ve) is inert (for

Test setup for electro etching salt solution with different metals. Laboratory power supply, time switch, glass jar with salt solution, electrodes of each metal tested in turn. Fresh salt solution for each test



instance platinum or carbon) it will not react with the Chlorine ions, and the gas will be given off as bubbles and can be separated and collected. The positive Sodium ions will react with water rather than with the negative metal of the cathode (explained below) releasing hydrogen as gas. The water (H_2O) loses an ion of hydrogen leaving HO which combines with the Sodium to make Sodium Hydroxide (Caustic Soda).

If the anode is a metal plate to be etched then the -ve Chlorine ion combines with the etched +ve metal ion (charged by the current) to produce a Chloride, and most of the Chlorine is not released as a gas. For example, a Copper anode plate will be etched by loss of one Copper ion which bonds to two Chlorine ions, making Copper (II) Chloride ($CuCl_2$). Then the soluble Sodium Hydroxide will react with the soluble Copper Chloride to make insoluble Copper Hydroxide, and soluble Sodium Chloride (by exchange of ions). Being insoluble, the Copper Hydroxide will be seen first as a slight yellow green cloudiness in the solution, and then in time will sink to the bottom as a solid powder precipitate. Similar

Test – etching copper electrodes in brine :175 gms.salt in 2.3 litres distilled water, 3 volts x 0.8 amps for 30 mins in 3 stages. Anode plate stopped with varnish brush strokes



After etching has stopped the precipitate starts to fall to the bottom as it is formed by the reaction between cupric chloride and caustic soda

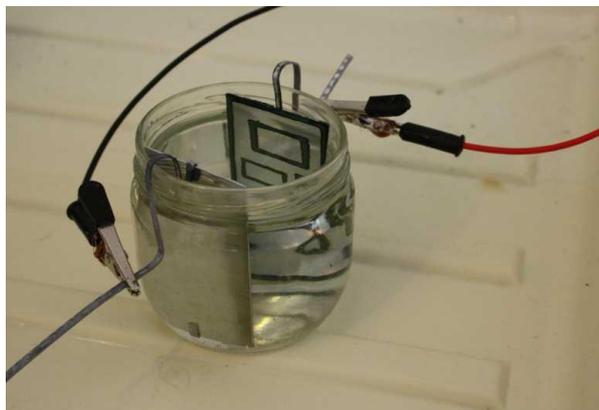


reactions are produced by Zinc, Iron, or Aluminium used as anodes, producing Zinc(II)Chloride, Iron(III)Chloride, or Aluminium(III)Chloride, and then reacting with the caustic soda, to leave Zinc Hydroxide (grey), Iron Hydroxide (black), or Aluminium Hydroxide (white).

In practice, depending on the current and area of metal surface, a foam can be produced on the surface, which is hydrogen in bubbles of the soluble metal Chloride and caustic soda (see illustration).

Also while the current flows the formation of the precipitate seems to be slightly inhibited, so at that stage the electrolyte is a mixture of more or less toxic solutions. After the current is turned off, the precipitate forms more rapidly if the foam is stirred into the electrolyte and then the liquid clears slowly. Because of the precipitate a plate flat on the bottom of a tray with a grid cathode would etch very unevenly. Even with a vertical Zinc anode the Hydroxide forms a very hard layer on the etched surface which inhibits further etching after a while. Etching steel plates produces very varied results depending on the other metals that are alloyed with pure iron.

Etching zinc plate in brine – bubbles begin to form at cathode but no deposit is formed at first.



Etching zinc – bubbles streaming from cathode towards anode and water beginning to go grey.



Stainless steel should not be used as an anode, because it is very resistant to being etched, or in other words, it will not combine easily with the Chlorine, which is either given off as a gas, or reacts with the caustic soda to produce Sodium Chlorate, which is a weed killer now banned for use in the European Union.

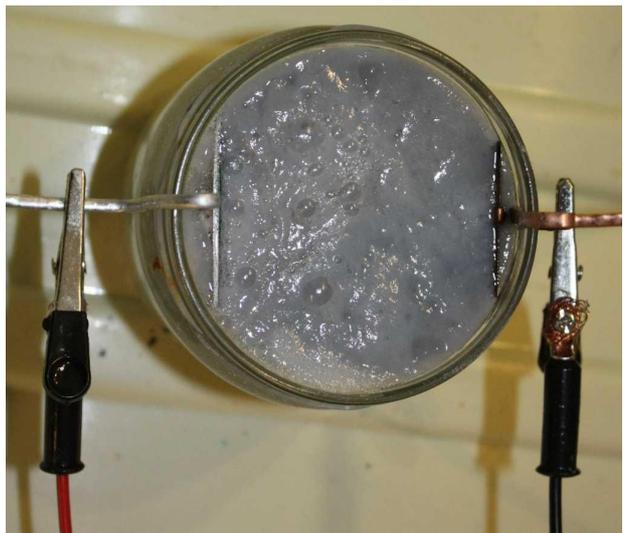
After the etching has finished and the steel plate removed a dark brown crust remains on the surface and gradually the hydroxide precipitate forms and falls to the bottom



Etching steel (iron anode) in brine – black foam forms on the surface very rapidly. The bubbles are formed by hydrogen in caustic soda and ferric chloride.



Etching Aluminium anode in brine – the aluminium is slow to react with the chlorine which can be seen as bubbles being given off the anode plate and a thick foam forms very rapidly on the surface trapping bubbles of hydrogen and chlorine.



On removal of the electrodes gently the foam shows a crust of ferric chloride which has not yet reacted with the caustic soda

Slowly the precipitate forms as a heavy cloud that floats down to the bottom.



The following detailed descriptions of the chemistry and health hazards are derived from references in chemistry textbooks, internet sites (linked) and from direct observations of tests and from the basic equations..

Copper(II) Chloride

Electrolysis of Sodium Chloride with Copper electrodes

Electrolysis of aqueous Sodium Chloride with Copper electrodes produces (among other things) a blue-green foam that can be collected and converted to the hydrate of Copper(II)Chloride (CuCl₂).

In theory, while the current flows the Copper anode is etched, releasing 2 Copper anions (+ve) which combine with one Chlorine cation (-ve) giving Copper(II)Chloride, which is soluble in water. But Copper Chloride reacts with the caustic soda to give a precipitate of Copper Hydroxide. This shows as a green insoluble deposit.

Addition of Copper Sulphate and Sodium Chloride (« Saline Sulphate etch »)

There are multiple ways of making Copper Chloride, one of them is by adding Sodium Chloride (table salt) to Copper Sulphate in the right proportions.

The chemical reaction here is a exchange of ions.
 $2\text{NaCl}(\text{aq}) + \text{CuSO}_4(\text{aq}) \rightarrow (\text{Evaporation}) \rightarrow \text{CuCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq})$

Theoretically it is possible to get 115 grams of Copper Chloride using 100 grams of Sodium Chloride and 213 grams of Copper Sulphate pentahydrate (CuSO₄ 5H₂O). For a full explanation of this process see:

<http://www.paulslab.com/experiments/making-copper-chloride.html>

This reaction requires more examination, in particular when Saline sulphate etch is used for etching zinc, steel or aluminium, in particular the secondary reactions after the copper has been precipitated and the metal has combined with the sulphate ions. For instance does aluminium sulphate exchange ions with sodium chloride to produce aluminium chloride + sodium sulphate ?

Health Hazard Information for Copper(II)

Chloride

Eye: Causes eye burns. Exposure to particulates or solution may cause conjunctivitis, ulceration, and corneal abnormalities. Contact with the eyes may cause corneal damage.

Skin: Causes skin burns. May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material. May cause skin rash (in milder cases), and cold and clammy skin with cyanosis or pale color.

Ingestion: May cause severe and permanent damage to the digestive tract. Causes gastrointestinal irritation with nausea, vomiting and diarrhea. Causes gastrointestinal tract burns. May cause perforation of the digestive tract. May cause hemorrhaging of the digestive tract. The toxicological properties of this substance have not been fully investigated. May cause systemic effects.

Inhalation: May cause ulceration and perforation of the nasal septum if inhaled in excessive quantities. Causes chemical burns to the respiratory tract. Inhalation of fumes may cause metal fume fever, which is characterized by flu-like symptoms with metallic taste, fever, chills, cough, weakness, chest pain, muscle pain and increased white blood cell count. The toxicological properties of this substance have not been fully investigated. Aspiration may lead to pulmonary edema. May cause systemic effects. Can produce delayed pulmonary edema.

Chronic: Prolonged or repeated skin contact may cause dermatitis. Effects may be delayed. Individuals with Wilson's disease are unable to metabolize Copper. Thus, Copper accumulates in various tissues and may result in liver, kidney, and brain damage.

<http://avogadro.chem.iastate.edu/MSDS/CuCl2-2H2O.htm>

Zinc (II) Chloride

Electrolysis of Sodium Chloride with Zinc electrodes

Using Zinc electrodes in an electrolyte of Sodium Chloride a similar reaction to the above can occur producing aqueous Zinc Chloride (ZnCl₂) and aqueous Sodium Hydroxide (NaOH) and Hydrogen gas.

$\text{ZnCl}_2(\text{aq.}) + \text{NaOH}(\text{aq.}) \rightarrow \text{Zn}(\text{OH})_2(\text{ppt.}) + \text{NaCl}(\text{aq.})$

The hydroxide is very quickly generated and forms a deposit adhering strongly to the anode creating a very uneven etch and stopping the etch completely in areas. After a while the chlorine cannot react with the zinc any longer and is given off as a gas with its attendant hazards (see chlorine hazards).

Health Hazard Information

Potential Acute Health Effects: Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (corrosive, permeator), of eye contact (corrosive). The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

<http://www.sciencelab.com/msds.php?msdsId=9927328>

Ferric Chloride

This is well known as a mordant for copper in the electronics industry, and for a period was used as a mordant by printmakers and metal workers before its dangers were known, especially used as a mordant for zinc.

Electrolysis of Sodium Chloride with Iron electrodes

Using iron as the electrodes in the electrolysis of salt solution will produce negative chlorine ions, which combine with positive iron ions at the anode producing Iron(III)Chloride and etching the iron. At the cathode Sodium Hydroxide and hydrogen gas are produced.

When aqueous Ferric Chloride is allow to react with Sodium Hydroxide, reddish brown precipitates of ferric hydroxide are formed and the Sodium reacts with the chlorine to produce Sodium Chloride . The hydrogen and some of the chlorine form a foam with the chloride as a brown scum on the surface inhibiting the reaction with the caustic soda.
$$\text{FeCl}_3(\text{aq.}) + 3\text{NaOH}(\text{aq.}) \rightarrow \text{Fe}(\text{OH})_3(\text{ppt.}) + 3\text{NaCl}(\text{aq.})$$

After the foam on the surface is stirred into the liquid the Ferric hydroxide settles to the bottom and after filtration dries as a black powder. Steel etching plates are alloys with other metals and the above reactions refer to pure iron. Steel alloys will differ depending on the reaction of the other metals in the alloy.

Using some kinds of stainless steel as the anode, which are very resistant to oxidation, inhibits the negative ions of chlorine combining with the positive ions of iron, and the formation of the iron(III)chloride, and so nearly all the chlorine is

given off as gas with its attendant hazards (see chlorine hazards).

Health Hazard Information

Iron(III) chloride is toxic, highly corrosive and acidic. The anhydrous material is a powerful dehydrating agent.

Although reports of poisoning in humans are rare, ingestion of ferric chloride can result in serious morbidity and mortality. Inappropriate labeling and storage lead to accidental swallowing or misdiagnosis. Early diagnosis is important, especially in seriously poisoned patients.

Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation. Slightly hazardous in case of skin contact (permeator). Corrosive to eyes and skin. The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering.

Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death.

<http://www.sciencelab.com/msds.php?msdsId=9924033>

[https://en.wikipedia.org/wiki/Iron\(III\)_chloride](https://en.wikipedia.org/wiki/Iron(III)_chloride)

Aluminium (III) Chloride

Using Aluminium electrodes in an electrolyte of Sodium Chloride a similar reaction to the above can occur producing Aluminium (III)Chloride (AlCl_3). But unlike copper and zinc, the aluminium is more resistant to oxidation, and chlorine is given off in greater quantities. Very slowly the aluminium chloride reacts with the caustic soda and a white scum of chloride bubbles form on the surface trapping hydrogen and chlorine gas. After the current is turned off, Aluminium Hydroxide slowly forms as a cloud in the solution rather than a deposit on the bottom. The Chloride remains as a scum on the top until it is stirred into the solution, releasing the gases.

Acute Health Effects

The following acute (short-term) health effects may occur immediately or shortly after exposure to Aluminum Chloride: Contact can severely irritate and burn the skin and eyes with possible eye damage. Inhaling Aluminum Chloride can irritate the nose and throat causing coughing and wheezing. Inhaling Aluminum Chloride can irritate the lungs causing coughing and/or shortness of breath. Higher exposures may cause a build-up of fluid in the lungs

(pulmonary edema), a medical emergency, with severe shortness of breath.

Chronic Health Effects

The following chronic (long-term) health effects can occur at some time after exposure to Aluminum Chloride and can last for months or years:

Cancer Hazard

According to the information presently available to the New Jersey Department of Health, Aluminum Chloride has not been tested for its ability to cause cancer in animals.

Reproductive Hazard

There is limited evidence that Aluminum Chloride may damage the developing fetus and affect male fertility in animals.

Other Effects

Repeated exposure to Aluminum Chloride may cause scarring of the lungs (fibrosis) and reduce lung function with symptoms of coughing and shortness of breath.

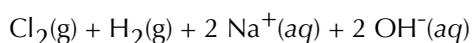
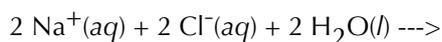
<http://www.sciencelab.com/msds.php?msdsId=9922851>

Synthesis of Sodium chlorate

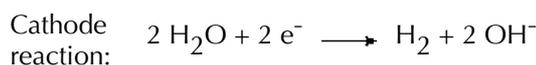
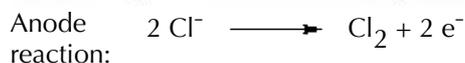
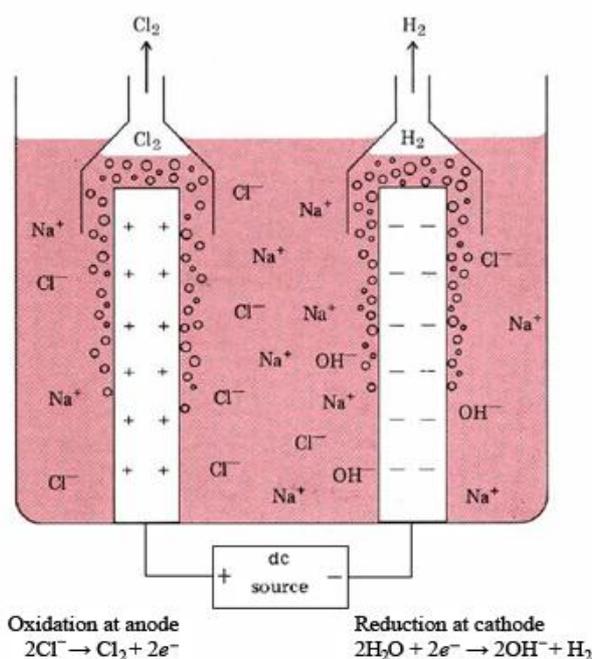
The [Chloralkali process](#) is an industrial process for the electrolytic production of Sodium chlorate. It can also be synthesized by passing [Chlorine](#) gas through a solution of [Sodium Hydroxide](#). It is then purified by [crystallization](#). If the Chlorine gas is not channelled and collected, but mixes freely with warm caustic soda, then Sodium chlorate is produced. Sodium chlorate is a very toxic chemical banned since 2008 in the European Union where it was used as a powerful weed killer.

Electrolysis of aqueous Sodium Chloride – technical description

Chlorine and Sodium Hydroxide (caustic soda) are presented together here, because industrially they are produced simultaneously by the same process, the electrolysis of brine (aqueous NaCl). These reactions assume electrodes of carbon. Other metals like platinum that resist oxidation may be used.



During electrolysis, Chlorine is formed at the anode, and hydrogen and Hydroxide ions are formed at the cathode.



Because the Cl_2 formed at the anode and the H_2 formed at the cathode can react explosively, they must be kept away from each other. Furthermore, the Hydroxide ions formed at the cathode can react with any Chlorine that remains dissolved in the brine. To keep the products formed at the two electrodes away from each other, a porous diaphragm is placed between the two electrodes in the electrolysis apparatus.

In the electrolysis of brine, water is reduced at the cathode. This occurs because water is more easily reduced than are Sodium ions. This is reflected in their standard reduction potentials, -2.71 volts for Na^+ versus -0.83 volt for water. At the anode, where oxidation occurs, the situation is not as clear. The standard oxidation potential of water is -1.23 volts, while that for Chloride ions is -1.36 volts. This means that water is more easily oxidized than Chloride ions. In spite of this, Chloride ions are oxidized at the anode, not water. The reaction that occurs is not what would be predicted by considering only the standard oxidation potentials because standard electrode potentials reflect equilibrium conditions, when no current is flowing. When current begins to flow, the distribution of ions around the electrodes changes, and the equilibrium electrode potentials no longer accurately apply. The potential of a cell depends on the magnitude of the current that is flowing through it. The difference between the equilibrium potential, at zero current, and the potential when current flows is called

overtoltage. The magnitude of the overtoltage depends on the composition of the electrode and electrolyte, as well as on the current. Generally, overtoltages are small, so predictions of electrode reactions based on standard electrode potentials are usually correct. However, in the electrolysis of aqueous Sodium Chloride, the overtoltage for the oxidation of water, which is a neutral molecule, is large enough to make it more difficult to oxidize than Chloride ions.

Health Hazard Information Chlorine

Chlorine gas is a pulmonary irritant with intermediate water solubility that causes acute damage in the upper and lower respiratory tract. Occupational exposures constitute the highest risk for serious toxicity from high-concentration Chlorine. Mixing of Chlorine bleach (Sodium hypochlorite) with ammonia or acidic cleaning agents is a common source of household exposure. As with all poisons, the dose determines the toxicity. Exposure to low concentrations of Chlorine for prolonged periods may have destructive effects, as might very short-term exposure to high concentrations.

Signs and symptoms

Symptoms may vary depending on the degree of exposure. Exposure possibilities include acute low levels, acute high levels, and chronic low levels. Low-level (3-5%, 1-15 ppm) acute exposure Most poisonings fall into this category and are caused by household exposure to low-concentration cleaning products. Manifestations are as follows:

- Eye tearing, nose and throat irritation
- Sneezing
- Excess salivation
- General excitement or restlessness

High-level (20%, >30 ppm) acute exposure
In addition to the symptoms seen with low-level exposure, high-level exposure may result in the following:

- Dyspnea: Upper airway swelling and obstruction may occur
- Violent cough
- Nausea and vomiting (with the smell of Chlorine in emesis)
- Lightheadedness
- Headache
- Chest pain or retrosternal burning
- Muscle weakness
- Abdominal discomfort
- Dermatitis (with liquid exposure): Corneal burns and ulcerations may occur from splash exposure to high-concentration Chlorine products
- Esophageal perforation

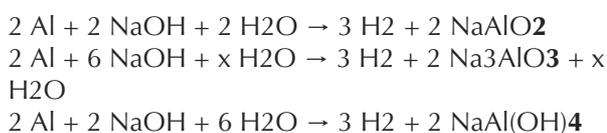
Sodium Hydroxide (Caustic Soda)

Like other [corrosive acids](#) and [alkalis](#), drops of Sodium Hydroxide solutions can decompose [proteins](#) and [lipids](#) in [skin](#), [eyes](#) or other [living tissues](#) via [amide hydrolysis](#) and [ester hydrolysis](#), which consequently causes [chemical burns](#) and may induce permanent [blindness](#) if it contacts eyes.[3][4] Solid alkali may also express its corrosive nature if there is water, so [protective equipment](#) such as [rubber gloves](#), [safety clothing](#) and [eye protection](#) should always be used when handling the material or its solutions.

Moreover, [dissolution](#) of Sodium Hydroxide is highly [exothermic](#), and the resulting heat may cause heat burns or ignite flammables. It also produces heat when reacted with acids.

The standard first aid measures for alkali spills on the skin is, as for other corrosives, irrigation with large quantities of water. Washing is continued for at least ten to fifteen minutes.

Sodium Hydroxide is corrosive to several metals, like [Aluminium](#) which reacts with the alkali to produce flammable hydrogen gas on contact:



Sodium Hydroxide is also mildly corrosive to [glass](#), which can cause damage to [glazing](#) or freezing of [ground glass joints](#). Careful storage is needed.

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