Introduction To The Electrolysis Of Rust

For some time I have had a need to be able to carefully remove rust from steel and iron artifacts and this page came into being as a result of my experiments into trying to achieve just this. I give a respectful nod to the various rust removal pages that were in existence before this one, and to which I was able to refer in the early years whilst doing my initial research; Some of those sites had ommitted detail which I felt the experimenter may need to be aware of, hence my decision to publicise my experiences and try to answer all the questions I had.

There are various obvious methods of rust removal, but these methods are unsuitable for very old or valuable artifacts as they tend to be destructive in use, meaning that along with the rust some of the base metal is also removed. Dissolving the rust with acids such as phosphoric acid or even vinegar can produce good results, but this process can remove surface features which may have been preserved in the rust. As I required a way of actually trying to salvage some of the rusted metal rather than just removing or dissolving it, these methods were considered inappropriate. This left the electrolytic method, also known as electrolysis, which involves using the passage of an electric current in an alkaline solution, or electrolyte, to do the job of trying to convert some of the corrosion products into a more stable form, whilst loosening the remaining corrosion by converting it into a loosely bound, easily removed deposit.

Please note that electrolytic cleaning is not suitable for non-ferrous metals such as copper, bronze, brass, pewter, tin or aluminium. The corrosion products found on these metals are rarely formed by electrolytic action and therefore the process cannot be reversed electrolytically. In the case of copper and tin alloys the treatment would be harmless, although aluminium could be adversely affected by the alkaline solution and so should not be subjected to this treatment. Don't make the mistake of thinking that rust electrolysis is akin to some magical, or quick and easy way of removing rust. Removing the loose converted rust once treatment has been completed is time consuming and quite messy, but if you are prepared to put in the effort, I believe the results are worth the trouble.

The idea of using electricity to convert rust back into iron is not a new one, and electrolysis has been used for metal restoration by collectors and archaeologists for decades and the results can be very impressive, with shiny metal being visible after proper treatment. The exact requirements, though, are sometimes poorly understood and the equipment often crude in design, although a simple setup constructed using household items is quite adequate as long as attention is paid to certain details. The equipment commonly suggested consists of simply a plastic container, some washing soda, steel plates and a battery charger, although some refinement to this equipment, in particular substituting an appropriate current limited power supply for the battery charger, will pay dividends in improved results, so more details on this later.

An Example Of What Can Be Achieved

An old horseshoe as it was when discovered near some old mine workings.

I feel it would be useful at this point to give an example of the kind of results that can be obtained using the electrolytic process and to describe the conditions under which they were achieved. After much searching for a suitable subject, I finally decided on an old horseshoe I'd found some months earlier. This horseshoe was probably well over a hundred years old and in a particularly badly corroded condition, having spent much of its time buried in the ground where it had developed a thick layer of flaky rust which had obliterated any surface features. To the left is a photograph of the shoe, and it is obviously in a very advanced state of corrosion and much damage had ocurred to the underlying metal. Note that no surface detail can be distinguished, with no nails or their holes visible. Attempting to clean this would represent an extreme test of the electrolytic process, but I decided to give it a try just to see what could be salvaged.

The shoe was initially prepared for treatment by using a small file to carefully remove a small area of rust on one edge in order to expose some metal, so that an electrical connection could be made using a crocodile clip. A fairly weak solution of twenty litres of washing soda was then made up at a strength of one heaped dessert spoon to every two litres - fifteen heaped spoonfuls in total, and a method of suspending the shoe devised. Once ready, the shoe was connected as cathode and a current limited to one quarter of an amp was applied and everything left to run for forty-eight hours. Once the allotted time had elapsed, the treated shoe was removed from the tub. It should be mentioned here that the solution had remained quite clear throughout and no detectable corrosion of the anode plates had occurred, this being due to the low current applied, and therefore the low voltage, and the enormous area of the anode plates relative to the cathode.


The same horseshoe after treatment using electrolysis.

The shoe, once out, was then soaked in water and rinsed under a tap to remove remnants of the solution. It was discovered that the outer layers of rust could now simply be pushed off using mild finger pressure to reveal a solid black and grey metallic core. I initially scrubbed the core using a plastic scrubbing brush, but found that it wasn't entirely removing the remaining black deposits and there were small persistent areas of red rust still adhering. At this point things were looking very encouraging indeed despite the obvious damage and erosion that had occurred to the shoe, as the positions of the nail holes were now easily visible, and it was possible to see the grain of the iron where it had been etched by the rusting process. I finally decided to give the shoe a gentle scrub using a wire brush, and this proved to be the answer as the black deposits were now easily removed revealing a shiny grey metal base. The nail holes themselves proved to be a bit stubborn, but I discovered that all but one could be pushed through using a small screwdriver, the remaining hole having the stump of a nail still in it. The shoe was finally given a rinse in warm water in order to heat up the metal, and quickly dabbed dry using toilet tissue whilst the retained heat of the metal rapidly dried off any remaining damp areas, minimising the chances of too much re-rusting. Finally, to protect the shoe from further corrosion, it was given a coating of light oil.

A Little On The Chemistry Of Rust

So, what exactly is rust? The chemistry involved in the formation of rust is rather complex and outside the scope of this page and my complete understanding, but a good site explaining the process in some detail can be found here:
Chemistry Of Iron.
A little basic information on the process may be of interest, though, so I'll outline it here. When an iron object is exposed to the air and a little moisture it undergoes a process known as rusting. This rust is the result of some of the iron combining with oxygen from the air to form new compounds, the exact nature of which depends on environmental conditions. In the simple case of a steel tool which has slowly rusted in a shed for example, there will probably be two forms of corrosion present which interest us:

1.) The outer layer of red rust is the surface we see and consists primarily of a compound with the chemical formula Fe_2O_3 (nH_2O), known as ferric oxide. This material takes up rather more volume than the metal it replaces and as a result it tends to flake away from the surface and if it occurs in mechanical devices, can seize up moving parts. The loss of this loose layer of rust represents a total loss of metal from the component which cannot be recovered.

2.) Underneath this outer layer of red rust may be found a harder, darker layer of material having an almost purple-grey appearance when freshly exposed. This layer is often in direct contact with the surface of the metal and is able to conduct electricity. It has the chemical formula Fe_3O_4 which is the same chemical composition as the mineral magnetite and is therefore sometimes referred to as such, although it is more commonly referred to simply as 'Black Rust'. As this material occupies the same volume as the original iron, surface features on the metal can sometimes be preserved in it with little distortion and as it tends to remain strongly bonded to the underlying metal, is fairly resistant to becoming detached and subsequently flaking off.

As the reaction involved in producing rust is an electrochemical one, it follows that it should be possible to somehow reverse the process using electricity, and this is indeed the case. As long as the polarity is correct with the subject matter connected as cathode, it is possible to chemically reduce some of the black rust back to metallic iron with a good bond to the original metal. During this process, much of the red rust is converted to Fe_3O_4 and becomes detached from the surface, aiding its removal when the conversion is complete.

The iron anode, or positive electrode, should be considered to be expendable and can be expected to rust as a result primarily of the presence of molecular oxygen combining with the iron. It is possible to use high grade stainless steel as an anode to reduce this, although the chromium present in stainless steel may produce poisonous chromium compounds in the electrolyte as it erodes which are considered dangerous and which will be illegal to dispose of down the drain in many areas. It is a good idea to avoid galvanised steel too, as it is important that no zinc, nickel, copper or similar metals get into the solution, as otherwise some plating of the cathode may occur.

During the reduction process, the iron is deposited in a manner which renders it highly reactive and it will develop a coating of rust surprisingly quickly if left wet - in a matter of minutes in fact, so rapid drying and the application of a protective layer is important. Finally, it is worth mentioning that the electrolyte itself is not involved in the reaction other than to conduct electricity and to provide an alkaline environment, although the level may drop slightly because of losses due to evaporation and the break down of the water into its component gasses. If this happens to any degree, plain water should be added to bring the level back up. The electrolyte may also become somewhat discoloured due to the rust products in suspension especially if higher currents are used, although this doesn't affect the process at all and there is no need to change the solution unless you wish to for aesthetic reasons.

Safety First

Before commencing with a description of the procedure some safety concerns should be mentioned.
Firstly, the electrolyte used is mildly alkaline and although not considered dangerous, prolonged contact with the skin should be avoided, and it *must* be kept away from the eyes. Obviously, if it gets onto your eyes, wash with copious quantities of water and seek medical attention immediately.

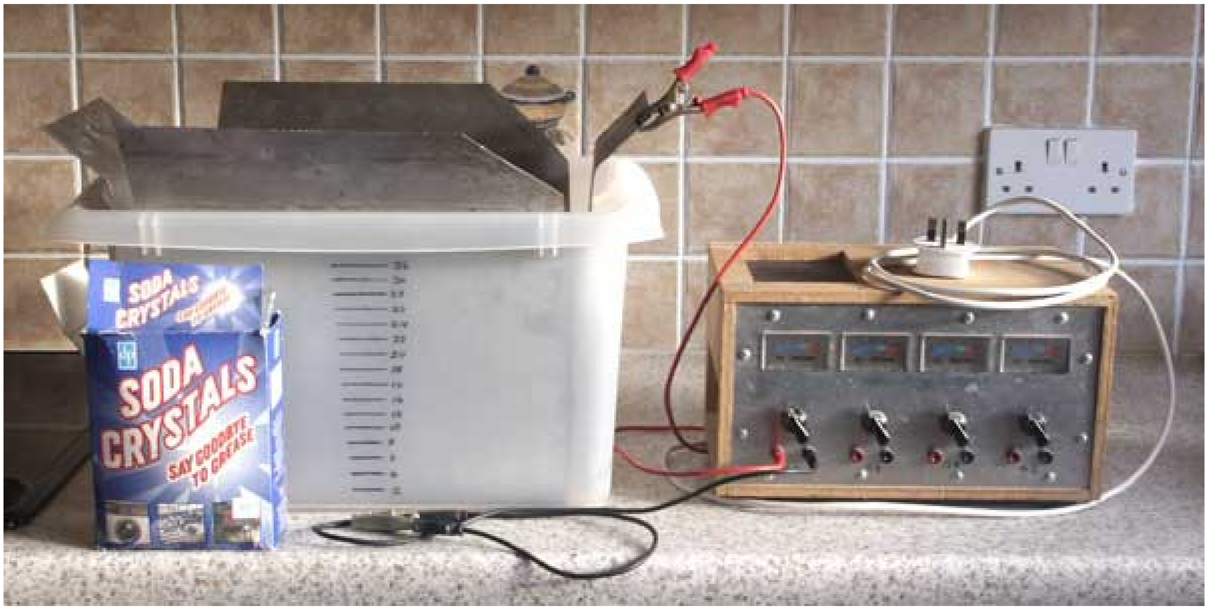
Secondly, the equipment involves the use of electricity. The voltage usually encountered, typically 10 to 15 volts, is not normally dangerous, although if contact is such that current flows across the body, for example an electrode in each hand, and the hands have been immersed in electrolyte for some time and are therefore highly conductive, even this low voltage could allow a dangerous level of current to flow across the chest area. Always switch off the supply before moving connectors. There is obviously also a concern with the proximity of the mains transformer to the liquid, so common sense must be used as regards the relative positioning of the components.

An important point concerns the production of explosive gasses. When current is passed through the electrolyte, both hydrogen and oxygen gas are evolved at the electrodes which when mixed, produces a highly explosive mixture. Ensure the procedure is conducted in a very well ventilated area, and avoid sparks or flames in the vicinity. Be aware that a spark will be produced if connectors are connected or disconnected whilst power is applied, and this could trigger an explosion. Always switch off the mains transformer before adjusting the electrode connectors.

My final safety note concerns the use of stainless steel for the anodes, and although I made mention of this earlier, I consider this is important enough to mention again. This approach may seem attractive because this anode material will not rust during use and I have seen this material suggested on some web sites. The big problem is that most stainless steels contain the metal chromium, and during electrolysis chromium compounds may be released into the electrolyte. Chromium compounds are highly poisonous and will be illegal to dispose of down the drain in many countries. I strongly recommend you do not use stainless steel for your anode material.

Method

Firstly, a suitable container for the electrolyte must be located which is large enough to totally immerse the item to be cleaned, and I recommend one made of plastic, as this is entirely inert and non-conductive.

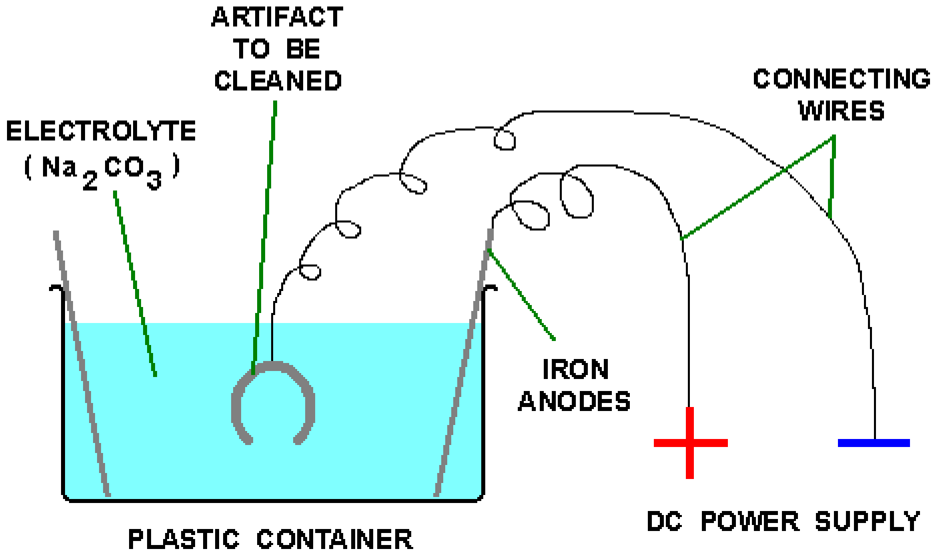


This photograph shows the equipment I currently use for small projects, showing the plastic
container, iron anode plates and my purpose built power supply which allows control over the current.

Suitable material for the anodes must be found, and 0.5mm - 1mm steel plate as used for car repairs is a good choice as it can easily be cut and shaped and is inexpensive, although it must not be galvanised or otherwise plated as this can cause the metal used for the plating, typically zinc, to form compounds in the electrolyte which could effect the final outcome. Metal plate is often coated in a film of oil and this protective layer should be removed with a solvent or detergent before use. These anodes should then be shaped to fit around the interior of the container ensuring part of each plate protrudes above the water level to enable a connection to be made. They should present a large surface area relative to that of the piece being cleaned and be able to 'see' most of the surface of the piece from all around to minimise areas of non-cleaning due to shadowing effects, as the current in the electrolyte tends to travel in direct lines rather than around corners. An anode made from a small piece of steel rod, for example, will work to a degree, but is less than satisfactory. It must be remembered that all the anode sections, if more than one are used, must be electrically linked to each other using clips and wire and it will be beneficial to include a plate across the bottom of the tub and ideally a gauze anode across the top as well to ensure the piece is completely surrounded by anode material. An alternative would be to simply turn the piece part way through the process to make sure any surfaces which had suffered shadowing effects are treated.

An alkaline electrolyte must then be made up, and I consider the best all-round option to be one to be a solution of sodium carbonate, Na_2CO_3, as it is reasonably safe and also readily available at many supermarkets under varions brand names. Be prepared for a slight precipitation of white calcium carbonate to be produced as the sodium carbonate reacts with the calcium ions present in tap water, especially in hard water regions, this having a tendency to first make the solution appear milky, then to coat the piece and electrodes with a snowy deposit as it settles out. If wished, the solution can allowed to stand for a day or two first to give this precipitated chemical time to settle to the bottom, and the clear solution decanted off, but it is unnecessary.

Suggested strengths for the solutions vary and any reasonable amount consistent with conducting electricity should provide adequate results, although I now regularly use a fairly strong 10% solution of washing soda. I did experiment briefly with caustic soda, and a suitable strength for this rather stronger chemical would be around 2%, although I noticed no difference in the results between the two. In order to demystify these quoted solution strengths, it simply indicates the weight of chemical contained in 100mL of solution, so for example a 10% solution would involve dissolving 10 grams of chemical in water and making up the final volume to 100mL. This obviously is the same as 1 litre containing 100 grams of chemical, and so on. If caustic soda is to be used, please bear in mind it will immediately damage the skin on contact, so appropriate protection must be used.



This diagram illustrates the components required
and the method of connection.

Some sort of power supply is now required. It must supply low voltage direct current, and battery chargers are often suggested for this purpose although due to the low resistance of the electrolyte large currents will flow causing a real risk of damage to the charger, or even fire. Even if this doesn't happen, the resulting current flow is far too high for good quality conversion, resulting in excessive anode erosion and the possibility of poor quality iron deposits at the cathode, and the relatively high voltage present across the electrolyte causes the water to slit up into its component parts resulting in large amounts of explosive hydrogen being evolved at the cathode. For prized pieces a little more refinement to the equipment is in order, but if a battery charger is the only current source available to you a good work-around would be to place a low wattage automotive lamp in series with the electrolysis tank in order to reduce the current flow to a low value, a 12 volt 2.2 watt lamp or similar being useful for limiting the current to around 200mA or so, and for higher currents, higher wattage lamps can be used - see the 'Special Considerations' section further down the page for more information.

This photo shows the equipment
actually in use cleaning
a pole trap.

When the time comes to connect up, observe the correct polarity - the piece to be cleaned MUST be connected to the negative terminal. It is vital that the electrodes are connected the correct way round, as failure to do this right will result in the gradual destruction of the piece. A good electrical connection to the piece is also required, and will involve removing rust from a small inconspicuous area down to shiny metal to effect a good contact. Pieces consisting of more than one component, for example a gin trap, must have all the separate components electrically linked to the cathode. This is most important, don't assume the components will be electrically linked simply by their close physical contact with each other. The photo to the left shows my equipment in use cleaning a fairly rusty pole trap. In the high resolution version of this picture you can see the way the trap is suspended in the solution and also that there are separate connections to the various parts of the trap. Also visible is the vast area of anode made up of four plates electrically connected together, and despite being in use at the time the photo was taken, the electrolyte is still clear with very few bubbles being produced. This is due mainly to the low current flowing, about quarter of an amp, resulting in only a small voltage appearing across the tub.

Once prepared and wired up, the piece can be suitably suspended and lowered into the electrolyte, ensuring it doesn't touch the steel plate anodes, and the power applied. Initially, there should be no bubbles coming from the cathode as the voltage differential should be insufficient to break down the water, being in the region of 1.8 volts, and if a higher voltage than this is observed, the current may be too high or there may be a poor contact to the piece. Once the reaction is complete however, a voltage rise to somewhat over 2 volts will be observed, along with the production of bubbles of hydrogen from the piece and this can serve to indicate the completion of the process, although it is a good idea to extend the time beyond this by a good 50% to ensure all is complete. After the appropriate time has passed, generally about 48 hours or so at quarter of an amp for a moderately sized piece, the power can be switched off and the piece lifted out and given an initial clean using a scrubbing brush or something similar, taking care to quickly dry it afterwards. The final stage is careful removal of the remaining rust using a small wire brush, and to protect against further corrosion a light film of oil should be applied. There is no risk of over-treating an iron artifact using electrolysis as bare iron is unaffected by the process and therefore the piece may be left in the electrolyte indefinitely as long as current continues to flow to give it protection from corrosion.

Certain pieces may consist of components made from a combination of metals or may have iron parts with zinc or nickel plating, or galvanising. Such plating and any brass components seem quite unaffected as long as they are given cathodic protection by being also connected to the negative terminal along with the rest of the artifact, but unfortunately any corrosion present on these non-ferrous metals also seems to be unaffected, and would therefore require a more conventional cleaning process. I have yet to do tests with aluminium, but for now would recommend you don't place any artifacts containing aluminium components in the solution.

Special Considerations

Always Have Current Flowing.

It is important to ensure that current is flowing whilst the piece is in the electrolyte, as it is the fact that it is the cathode in the circuit that protects it from corrosion. Should the piece be allowed to remain in the electrolyte without current flowing, it is possible, depending on its exact composition, that it will start to corrode, more so if the anode and cathode connections are shorted together, so if the power needs to be switched off, remove the components from the electrolyte also.

Voltage And Current.

Although using a battery charger as a DC power supply will get the job done on casual pieces and can produce reasonable results, for better results or valuable pieces attention needs to be paid to the current flowing. Put simply, if too high a current is allowed to flow from the start, the deposited iron will be very porous and possibly become detached from the surface and the rapid hydrogen bubble production can blast off rust which could possibly have been recovered using gentler methods. I therefore consider it necessary to limit the current to a maximum value based on the estimated surface area of the piece to be cleaned and although opinions vary as to the exact current density, I use and recommend a figure of approximately 1mA per square centimetre as this achieves a good rate of conversion while allowing the solution to remain clear and anode corrosion to be kept to a minimum. The process should be left to run for a few days at this level to ensure complete conversion, or until the small rise in voltage across the tub is observed.

Avoiding Rusting During Final Cleaning

The process of washing and scrubbing in water following the electrolytic treatment does allow the possibility of re-rusting of the piece before there is a chance to dry it completely, which can spoil the finish. One system I sometimes

use helps avoid this by removing water completely from the final stages, and the process, although cumbersome, works well and is outlined here:
Firstly, the piece must be taken from the cleaning tank and promptly placed in a tub of clean water where it is scrubbed with a plastic brush to remove much of the now loose rust and well rinsed to remove the washing soda. From here, it is then scrubbed and rinsed with Methylated Spirits (pure alcohol will serve) to remove the water along with more rust, and allowed to dry. Final cleaning work can now be performed on the dry piece, and when this stage is complete, the rust dust can be washed off using, once again, a solvent such as Methylated Spirits. Once this has evaporated, the piece can be given the final coating of oil or paint if desired. It is important to note that solvents can be dangerous if inhaled or handled, so these stages should only be completed outside with suitable protection and in accordance with the instructions and warnings relating to the specific solvents used.

Painting The Treated Item

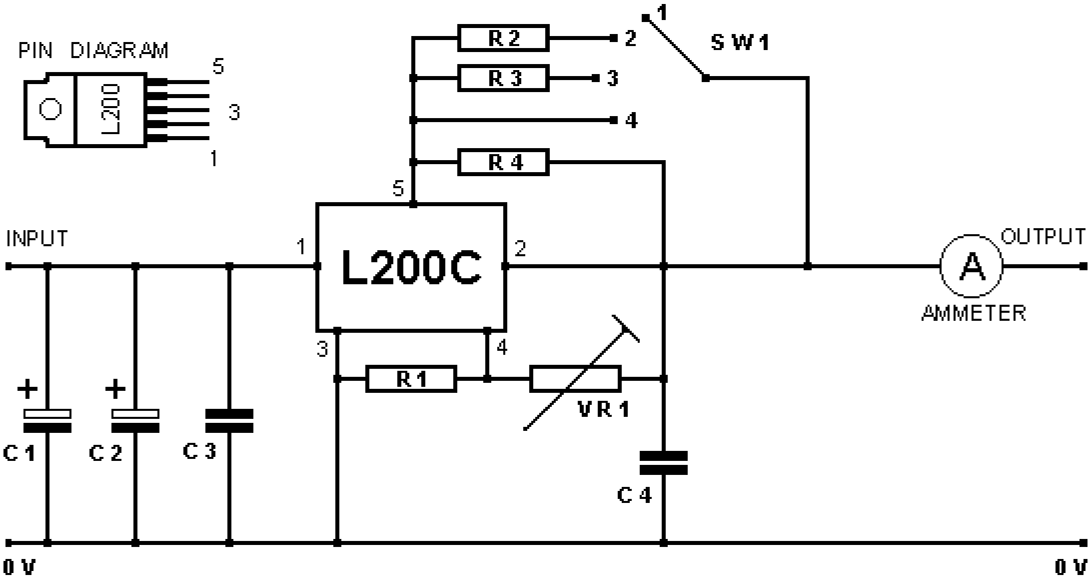
I have received a fair bit of communication regarding whether the surface of the treated metal is suitable for painting without further treatment. The truth is, I don't know as I have yet to try this - my pieces are either left as they are or given a coating of oil. I welcome opinions on this matter, and will try to conduct some experiments. I would suggest though that a coating of 'red lead' primer followed by a conventional metal paint would be fine and that there would be little chance of rust forming under the paint.

About Cleaning Non-Ferrous Metals

I have received quite a bit of correspondence concerning the cleaning of non-ferrous metals, such as copper, bronze, lead and silver. Some of these metals are often found in coins for example, so there is a requirement to attempt to clean artifacts made of these or similar metals. The corrosion products found on these metals is not formed by electrolytic action and therefore the process cannot be reversed electrolytically and damage may occur if an attempt is made to clean certain metals this way. Up to now my experience has mainly been with the conservation of land corroded iron or steel artifacts and so I am not in a position to offer much practical advice concerning the cleaning and preservation of such pieces, although there is a very informative site dealing with precisely this area, and although it is concerned mainly with artifacts recovered from a salt water environment, the information provided here should prove very useful: Conserving Underwater Archaeology.

A Purpose Built Power Supply

The idea of constructing a power supply could seem a daunting task for anyone not familiar with electronics, but for those interested, capable or who know someone experienced in such matters, I'll outline the details of such a supply in order that one could be built.



This diagram illustrates the components required to construct a regulated and current limited power supply suitable for small to medium rust removal projects. See table below for component values and purpose.

C1 , C2	2,200uF electrolytics for smoothing. Using two will half the ripple current on each.
C3	0.47uF decoupling for stability
C4	0.22uf decoupling for stability
R1	820 ohms
R2 , R3 , R4	Current limit resistors as required: 1 ohm = approx. 500mA 5 ohms = approx. 100 mA
VR1	10k variable resistor for voltage setting.
SW1	4 pole switch for selecting current.

This circuit represents a power supply built around the popular L200 voltage regulator chip, available from most electronic suppliers. It features an internal maximum current limit of 2 amps which will be more than enough for even fairly large pieces, and lower currents can be selected when required according to the values of the appropriate resistors, values for these depending on individual requirements and guided by the table above. Remember, slower is definitely better for this job, and my supply has a 100mA limit on its lowest setting, with 500mA and 1 amp as intermediate settings in addition to the maximum output of 2 amps.

Regarding the circuit diagram, R4 is permanently connected and when the switch is in position 1, is set to offer the lowest required current. Position 4 bypasses any limiting resistances and invokes the internal limit which is the maximum of 2 amps, whilst positions 2 and 3 are intended to offer intermediate current settings according to the resistances used, although it is entirely possible to incorporate more than the 2 intermediate settings indicated by using an appropriate switch, it is simply a matter of personal choice. A regulated voltage output can also be set using the variable resistor if needed and this will make for a more versatile piece of equipment, although being able to vary the regulated voltage is not necessary, and a fixed resistor of a value determined by experiment could be hard wired in to produce a voltage of around 12 volts.

The regulator package itself will need to be mounted on a large efficient heatsink to ensure it operates at a sensible temperature, and I recommend a specification of 2.2° per watt with a good air circulation to avoid problems when operating at full current or under inadvertent short circuit conditions. A transformer and rectifier assembly must be built in order to supply the above circuit with direct current at an appropriate voltage, and a transformer with a secondary winding of 12 to 15 volts at a rating of 50VA should be suitable, and a bridge rectifier rated at 5 amps is suggested. Obviously, high voltage components such as the mains transformer should only be fitted and connected up by a competent person, as the voltages involved are lethal. The inclusion of an ammeter is a luxury, but can give a useful indication of the actual current flowing as this may not always be at the current limit set, and such a condition may indicate poor connections to the piece, low strength electrolyte and so on. A meter with a full scale deflection of 2 amps would be ideal here. I also find it useful to be able to monitor the voltage developed across the tub, and as the voltage here rarely rises much above 2 volts, a low reading voltmeter is necessary for accuracy, and I find a portable digital multimeter gives the necessary accuracy at these voltages, whilst being immune to damage if it happens to be exposed to the full open circuit voltage.

Regarding the actual construction, the circuit layout is not critical and it can be constructed on a single sided copper laminate board or using a tag strip, but it is important that the decoupling capacitors C3 and C4 are fitted as close to the regulator's pins as possible to avoid instability problems, and that adequate heatsinking is employed. The case for this project can be almost anything the components will physically fit into as long as there are plenty of ventilation holes to keep the internal temperatures from climbing, and any high voltage points are shielded against being inadvertently being touched by inquisitive fingers or a probing screwdriver. If a metal enclosure is chosen, I suggest the case should be earthed.