Extra info For Chlorates

I INTRODUCTION

Electrochemistry, that part of the science of chemistry that deals with the interrelationship of electrical currents, or voltages, and chemical reactions, and with the mutual conversion of chemical and electrical energy. In the broadest sense, electrochemistry is the study of chemical reactions that produce electrical effects and of the chemical phenomena that are caused by the action of currents or voltages.

Sodium Chlorate

sodium Chlorate is the Chlorate that **is mass produced by industry in tonnage quantities.**

Its main use is in the making of ClO_2 (Chlorine Dioxide gas) for bleaching in the paper industry and others. Industrial setup's use a continuous method of making Chlorate as opposed to a batch process. The amateur will always use a batch process.

The starting material is NaCl (Sodium Chloride or common salt). Sodium Chlorate is very soluble. About 330 grams NaCl per liter of water is the starting solution. A saturated solution is OK, which can be made by heating the water and adding excess salt. When no more salt is dissolving, cool, and you will then have a saturated solution. Getting the NaCl to dissolve can be difficult but heating helps, not because the solubility of NaCl increased much with increase in temperature, but rather the heating stirs the solution.

Exactly what procedure you follow when making Sodium Chlorate is up to you. It really depends on what you want to do ultimately. If you are going on to make Sodium Perchlorate you may decide to separate the Chlorate and Perchlorate steps by separating out the Sodium Chlorate and then using this Chlorate in another cell to make Perchlorate. You may decide not to separate out the Chlorate and Perchlorate stages (saves labour) and simply keep running your cell without separating out the Chlorate as per US patent 3.493,478 (see the Sodium Perchlorate section) where a Fluoride is added to the electrolyte. Persulphate and Chromate's can also be used. (Chromate's are not compatible with Lead Dioxide).

Theses additives stop Chlorate and Hypochlorite being reduced (converted back to Chloride) at the Cathode.

Chromates also protect some types of cathodes (Iron, Steel, Nickel) against attack my Hypochlorous acid in the electrolyte. You need a Lead Dioxide anode to run from Chloride all the way to Perchlorate as wear rates on Pt may be too high. Wear rates on Graphite will be huge and simply not practical.

If you are making Potassium Chlorate (from the Sodium Chlorate) you can simply run your cell for the required run time and take out a crop of K Chlorate by adding KCl and start running the cell again.

Cost of making chlorate

People have argued that it costs a lot of money on power bills to make chlorate. The cost is small.
Assume we are going to make one KG of Na Chlorate, thats 9.93 moles. The following data is needed.

1) One mole $NaClO_3$ = 106.5g.
2) One mole of electrons = one Farad = 26.8 Ah (Ampere hours).
3) It takes 6 electrons to make one molecule of chloride into one molecule of Chlorate. (2 electrons per oxygen), that means it takes 26.8 X 6 = 160.8 Ah to make one mole of Na Chlorate (assuming 100% current efficiency, 100% current efficiency means that every electron that goes into the cell will do what we would like it to do, ie. help to 'stick' an oxygen onto a Chloride).
4) We will assume that we will get 50% current efficiency which is easily achievable using a amateur set up with no pH control.
5) Power supply wastes 20% of the power that it delivers, (thats a bad supply).
6) Assume that there is 6 volts across the chlorate cell. There will be no more than this with a sensible cell.
7) Assume the price of power is 8 pence per KWh (kilo watt hour). The KWh is referred to (usually) as a unit of power. Thats approx. 12 cents per unit. It may be different in your area.

We are making 9.39moles (1kg) of Na Chlorate so we need 9.39 X 160.8 Ah = 1510 Ah of electrons to make 1KG(100% efficiency) need to be checked
Assuming 50% current efficiency means that it will take twice this ie. 3020 Ah

(Ampere hours).
If we run the cell at 10 amps this means we must run the cell for 302 hours to get one KG of Na Chlorate.
We have 6 volts across the cell so we have a power usage in the cell of 6 V X 10 A = 60 watts.
Assuming that the supply wastes 20% of the power it delivers this means we have 72 watts of power being dissipated in the total set up.
72 WATTS for 302 hours = 21744 watt hours, = 21.744 KWh = 21.744 units.
Assuming that the price of power is 12 cents per unit this means the power cost is an (incredible!) 12 X 21.744 = 261 cents ($2.61). (worst possible case)

The voltage across the cell will probably be much less than 6V, and may be as low as 3.6V. The power cost in the States is about 5.5 cents.
The represents a power cost of about 57 cents per KG Na Chlorate pro ducted.

If you can buy Na Chlorate by the barrel it will be cheaper that above but not everybody has access to barrels of Chlorate. The cost above is not the total cost of course you must buy salt (fairly cheap), you must also allow some power for boiling/evaporating solutions etc, but Chlorate is not expensive to make.

Power supplies

The supply must be a DC supply with a current capability of at least what you want to run the cell at and a voltage somewhere between 3.5 and 10 Volts. The positive is connected to the Anode and the Negative to the Cathode.
The power supply for making Sodium Chlorate or Perchlorate can be quite a crude affair or it can be as sophisticated as you like. It would be nice to have a supply **that has a programmable current**. This ideal supply would also have a fully smoothed output, built in Voltage and current meters, a Coulomb meter (measures Ampere hours) and be efficient.
To buy a supply like this would be expensive. A battery charger can be utilised as a power source. You may have to use the six volt setting as the current may be too high if you use the twelve Volt setting. It should be noted that the '12 volt' setting may not be 12 volts when you connect the charger to the cell. Chargers have bad Voltage regulation (an necessity when it comes to charging batteries and an advantage in our application) and the voltage will drop when you connect it to the cell. It will depend on the actual charger type and size of charger. If your charger has only a twelve volt setting and it is driving too much current into the cell you

could consider **putting two cells in series**. You can also use resistors or diodes to lower the current into the cell
With battery chargers it is difficult to measure the current going onto the cell as they do not supply a fully regulated (smooth) DC current Voltage. You would need a true RMS meter to get a proper reading of the current going into the cell. Accurate measurement of current is not that important **but you will need some indication of what the current is if you want reasonable accuracy regarding run times.** If you can get a reasonable battery and connect this to the charger/cell set up this will have the effect of smoothing the current/voltage. Then an ordinary multimeter will give reasonably accurate measurements of the current.
An AC welder is a good supply to use for a cell but the output MUST **be rectified before applying it to the cell.** A DC welder will do too. The current will not be smoothed. The welder will be a constant current generator but its lowest current setting may be too big for your set up **(size of Anode and cell volume)**. There is also the disadvantage of the welders high open circuit voltage. When you disconnect the welder it's output voltage will rise to maybe 80V. If, when your cell is running, one of the connections going to the Anode or Cathode gets corroded the voltage will rise across this bad connection as the welder forces in the constant current. This will lead to the connection failing by becoming red hot. This may permanently damage your Anode or perhaps cause a fire/explosion. A welder makes a good supply for an established cell and setup that has good connections, but it is a bad supply for experimenting with.
Computer power supplies are a cheap source of power for the cell.
A good transformer can be made from a microwave oven transformer (MOT).

See here for some info rewinding MOT's.
A good way to control the current going into the cell is to use two variable voltage transformers as per the diagram below. First the cell is run for a while at a sensible current so as to warm it up. Variac No. 2 is set to point A1. The voltage across the cell is measured at the current you want going into cell. The supply is disconnected and the voltage at the output is increased somewhat (a few volts) by turning variac 1. Only use a few extra volts here as a too large an open circuit voltage can lead to heating problems at electrical joints if the joint corrodes. The supply is now reconnected and the current you want going into cell is set by

adjusting variac No. 2. This will give a situation whereby if the Resistance of the

cell rises a small amount the current going into cell will remain constant.

If you only have one variac put it on the input of the transformer to control input (and therefor output) voltage.

It should be noted that the current/voltage going into your cell with the power supplies above will not be a smooth DC current/voltage. A capacitor can be connected across the cell so as to smooth the current and voltage. It should be noted that using too large a capacitor can lead to problems as the transformer may not be able to supply the high peak current pulses that are characteristic of capacitor smoothed supplies. The good old unsmoothed current does the job OK, but it is hard to ascertain what the actual EFFECTIVE current going into your cell is. It would be nice to have a true RMS meter. If you are trying to do accurate measurements of current efficiency and run times you would need to smooth the supply properly or get a true RMS meter.

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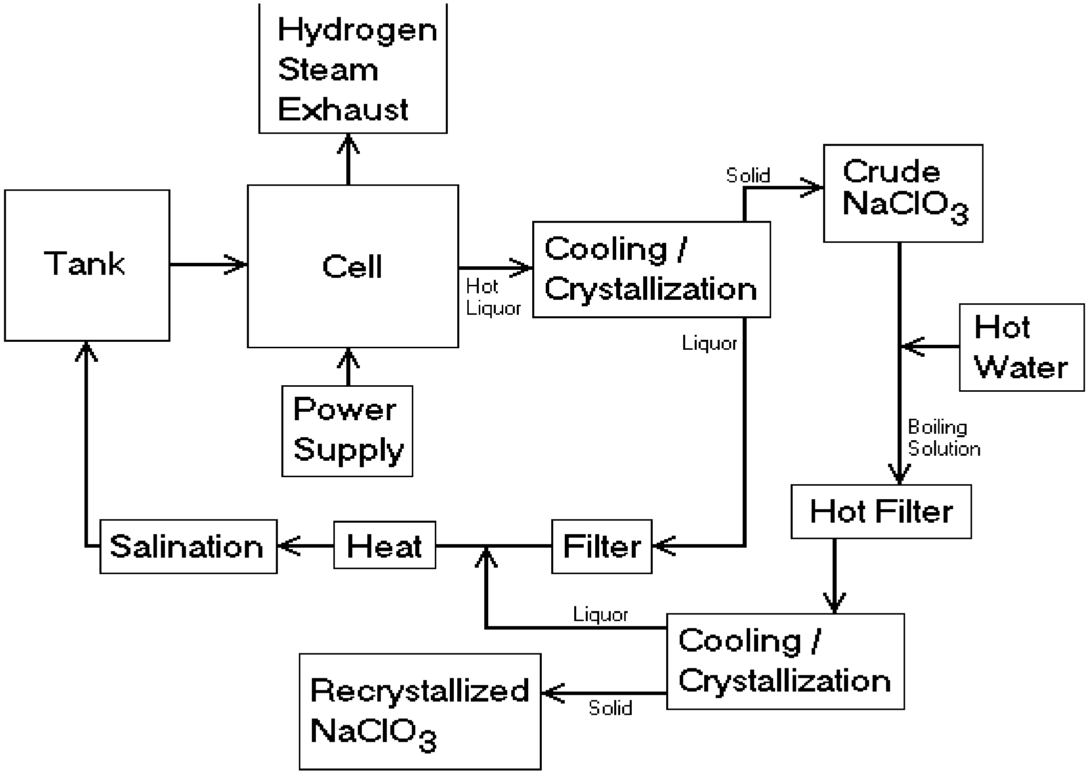
Sodium Chlorate Production

This page expands on the last cell I posted about. It's still going good (as of 7/8/07 -- three months!), though the graphite took a bit hit of wear (maybe 1/8" off the thickness) when I let it run too long. Of interest, I upgraded the power supply. I now have 6VDC available at 60A load. That's a bit much for a cell, so I connected a ballast resistor -- a chunk of steel wire -- in series, which drops cell voltage to a more suitable 4V. I also installed an ammeter, which probably came from a battery charger. It isn't very accurate, but it shows around 60 amperes to be a typical current, and I have no reason to doubt that. The cell now reaches 65°C, which is hot enough for better efficiency, or something. Fed up with bad connections, I also copper plated the top four inches of the graphite anode. (That reminds me, I need to write a page on that.) It is corroding, due to some particularly malignant pores going through this bar of graphite, but that's not much of an issue as in a few months I can merely peel off what's left and replate it, at the expense of a few days downtime.

I've been running pretty well constantly for the last few weeks, and have come up with a few more pounds of sodium chlorate. I estimate I am producing 2 pounds per week. How much is that? Well, 2 pounds is about one kilogram. $NaClO_3$ is 23 + 35 + 3*16 = 106 g/mol molecular weight, so I have about 9 moles per week. It takes 6 mol electrons to produce 1 mol of the stuff, so, at 100% efficiency, I must be using 54 moles of electrons per week. But 60 amperes for one week is 420 A-days, or about 10 kAh. (Which, at a typical 7V supply (that includes losses), is 70 kWh, or at $0.10/kWh, some $3.50 per pound...if I were paying the electric bill.) Since one faraday is 96485 C/mol, or 26.8 Ah/mol, 10 kAh therefore is 376 mol electrons, or 63 mol $NaClO_3$. But I'm only making 9 mol/wk. Holy crap, that's 100 * 9/63 = **14% efficiency!** I've never heard of anything so atrocious.

To remedy this problem, I think I'm going to get rid of the nasty liquor I've been using. It's kind of foamy and yellow, a lot like well, bleachy-smelling urine, or beer. I suppose there's not much difference between those analogies... It would be effective to dry it out, then wash with hot water to recrystallize the $NaClO_3$, leaving the NaCl and impurities behind. Twiddling the pH may also have some effect, though transition metals (I would suspect Fe and Cr) tend to precipitate in high pH, which is what this is, which makes absolutely no sense to begin with. There must be some complex at work, but chloride has been up and down lots of times with no change, and though the chlorate ion has a lone pair (like ammonia and other ligands), it's tightly held by the three other oxygens on the molecule. The pH isn't sooo high that something like chromite could be present. And that's just those...who knows what else is present, sapping precious efficiency.



Anodes

Anode Overvoltage
Overpotential or Overvoltage refers to the excess electrical potential over theoretical potential at which the desired element is discharged at the electrode surface.
It will obviously vary with the different anode materials. It also varies from electrolyte to electrolyte given a fixed anode material. It also varies with current density, age, temperature etc. For Chlorate making we would like an anode with a low Chlorine overpotential and a high(er) Oxygen overpotential. Because Amateur cells are (usually) not pH controlled, we also need an Anode material with a low overpotential for the Oxidation of Hypochlorite ion (the 'second' reaction, see below).
For Perchlorate making we want a material with a low potential for the 'discharge

of the Perchlorate ion' and a high Oxygen overpotential. The higher the Oxygen overpotential the better because it means that Oxygen will not be made at the Anode. Oxygen forming at the anode is a leakage current we do not want and is one of the reasons for not getting 100% current efficiency when making (Per)Chlorate. It also wears the Anode.

Catalytic acitivity of Anode

When making Chlorate in a non pH controlled cell there is the further complication of the 'second' reaction that must take place at the anode surface (after Chlorine has been produced) in order to make Chlorate (see Cell Chem. section). In industrial cells a different reaction takes place in the bulk of the solution as the pH is favourable for the appropriate species to be present in the proper ratio in the liquid for this so called 'bulk' reaction to happen. The 'second' reaction is ClO^- (Hypochlorite ion) being made into Chlorate at the Anode surface. This reaction is sometimes referred to as 'making Chlorate by electricity'. In industry it is very undesirable and is avoided. In amateur non-pH controlled cells it is the way all the Chlorate gets produced. The Anode therefor (in the non-pH controlled cell) must have Catalytic activity capable of both evoluton of Chlorine and Oxidation of Hypohlorite ion. Magnetite has poor to no activity for the Oxidation of Hypochlorite ion. Pt, C, MMO and MnO2 are OK. PbO2 ??

Cell Anodes

Material	Comments
Graphite or Carbon	Graphite is a dense form of the element Carbon. The terms Graphite and Carbon are sometimes used interchangeably. Graphite or Carbon are a good Anode material but you must not let your cell temperature get above 38 Centigrade and you must not let the Chloride concentration in your cell get low or the Graphite will be rapidly eroded. Dense Graphite is much better than Carbon (softer and more porous than Graphite) as far as lasting is concerned. Graphite or Carbon can be make to last longer by impregnating it with linseed oil as it stops it from shredding. Dense Graphite cannot be impregnated with the oil. Proper

	pH control helps too. Carbon can be purchased at welding supply shops in the from of Gouging rods, and it is very advantageous to treat it with Linseed oil to make it last longer. Dense Graphite can be purchased at engineering supply shops where it is used in EDM's (Electro Discharge Machines). Battery Carbon rods can also be used. Graphite or Carbon should not be used in a Chlorate cell that is above 38C (better below 30C or lower) or that has a Chloride concentration lower than 100g/l or it will erode rapidly. Low Chloride concentration is the worst parameter (by far) that will cause erosion. The current density used on Graphite in Industry is between 33 & 43 mA per square cm. Keep it low to avoid erosion. It should be noted that as Graphite rods erode their surface area gets less and less. Therefor the current density will increase and increase as will erosion. Bear this in mind when using Graphite. Figures from Industry regarding Graphite erosion are quite impressive. Graphite will NOT make Perchlorate unless in a cell with a diaphragm.
Lead Dioxide	A good Lead Dioxide Anode will last a long time and it is not effected by high temperature's (within reason, below 55C) or low Chloride levels. If Chloride levels get low (below 10%, or 100g per Liter) Perchlorate will start to form. You cannot use Chromate's with a Lead Dioxide Anode which in turn means that you should not use some types of Stainless Steel as they may corrode a small amount and introduce small amounts of Chromate into the electrolyte, 316 is OK. Chromate's lower current efficiency by forming a thin layer on the surface of the Anode. Anode current densities of 80mA to 300mA per square cm can be used. The lower current densitys are used in Chlorate cells as current efficiency will suffer if a high current density is used. High current densitys do not effect current efficiency in Perchlorate cells, in fact it improves CE. Lead Dioxide is the *HOLY GRAIL* of Anodes. It can be let

	run and run until all Chloride has turned to Perchlorate which saves a great amount of labour. It will lower the Chlorate to a low level. Lead Dioxide Anodes that are reliable are problematic to make for the Amateur.
Platinum	Platinum is good but is expensive. It will make Perchlorate's. It will corrode if Chloride levels are let drop down too far in a Chlorate cell. It will also corrode if used in a Perchlorate cell that has a low Chlorate level in it. If using this anode to make Perchlorate start with a cell with zero (0.00%) Chloride in it and use Dichromate to protect the anode. Pt has been plated onto valve metals (Ti, Ta, Hf, Nb) for use in Industry. If purchasing a plated Valve metal anode be aware of the coating thickness as some are very thin. Pt depths of 1.27 to 2.54 micron have been reported for Chlorine production anodes with wear rates of 0.5 grams per ton Chlorine (Metals Handbook). Pt/Ir alloys have been used where current density's as high as 750mA per square cm were used. It is not too temperature sensitive as far as corrosion is concerned, keep below 40C. Current densities can be high at 300mA and up, 600mA has been use in a commercial cell for Perchlorate. Wear rates of 500 to 220mg/Tonne have been stated. Smooth Pt, for example wire, (same as electro deposited Pt) is preferred as its wear rate is less that other forms of Pt, like for example thermally deposited coatings. Pool Chlorination anodes are sometimes Pt based (as opposed to MMO).
DSA or MMO	MMO (Mixed Metal Oxide (formally know as DSA (Dimensionally Stable Anode))), made from a range of Noble metal oxides + Ti oxide with Valve metal Oxides on Valve metal(Ti, Ta, Hf, Nb) substrates using a large variety of processes. Used by ALL Chlorate Industrial setup's nowadays. They do not like to be used in electrolytes where the Chloride level has been let drop low (<30g/l). DSA are less expensive than Platinum. They can be used used at

	relatively high current densities, 300mA per square cm. Probably better to keep below 150 or less. There are a huge amount of MMO Anodes on the market. The corrosion prevention industries use them where they are used in very low Chloride situations at low current density. MMO will not make Perchlorate AFAIK though some types may be capable of making Perchlorate. MMO should not be operated at high temperatures. Pool chlorination anodes are mostly MMO anodes though sometimes they are Pt based.
Magnetite	It has been used to make Chlorates in Japan (and India) up to (and beyond?) 1971. It will make Perchlorate. They last a long time in a Chlorate cell even if there are low Chloride concentrations. Current density's up to 30mA per square cm have been used in Industry. Current density is not limited by erosion concerns but rather by economic reasons. Current efficiency suffers a lot. High temperatures do not erode them, up to 70C. They will not lower Chloride concentration to low levels possibly because of their surface electro chemistry. The Magnetite anode has very low current efficiency when used in a Chlorate cell that in not pH controlled (3%CE). If Magnetite is to be used to make Chlorate, pH control is necessary. CE of approx. 61% was obtained in a small (520ml) amateur cell that was pH controlled. This same cell produced Perchlorate when Chloride concentration decreased. Ferrite's, as used in high frequency transformers and radio aerials, will not make Chlorate as they are not conductive.
Manganese Dioxide (MnO_2)	This anode will make Chlorates very successfully. In a Perchlorate cell it erodes. This anode is easy to make and has been shown to work in a Chlorate cell for weeks. Use at approx. 50mA per square cm.
Spinal Cobalt Oxide (Co_3O_4)	This anode will make Chlorates and Perchlorates but it will not stand up to Chlorate cells for more than a few days. It only lasts for hours in a Perchlorate cell.

Semiconductor Anodes	This type of anode is mainly concerned with Antimony Doped Tin Oxide (ATO). It is not a very successful Chlorate or Perchlorate anode. Tin Oxide doped with Bi Oxide is stated to be useful for Perchlorate production.
Titanium, Gold, Tungsten, Tantalum etc	Theses metals will not make Chlorate or Perchlorate.
Lead	Lead will make Chlorate and Perchlorate as (badly adhering) Lead Dioxide forms on its surface. Be prepared for a toxic mess as the Anode will corrode from the beginning.

The Sodium Chlorate cell

One could talk for a very long time indeed about the design for a Sodium Chlorate cell.

The amateur usually finds it difficult to know where to start when it comes to setting up a cell. It can be very confusing when one reads all the information available on the topic. Most of the reading material is geared toward the industrial producer (or sometimes the scientist who is studying the subject) who will have a different set of constraints forced upon him when compared to the amateur. The amateur will not be too sure how much quantity of product to make, how much money, time, effort and space to allocate to the project. Very often the starting point will be the power supply that is to hand, or the Anodes that can be made or purchased easily . Sometimes it will be decided to make a certain amount of product per time and having decided this go on to obtain Anodes and a power supply.

The amateur will not be terribly interested in making the cell as small as possible, getting maximum current or power efficiency or having the smallest possible voltage across the cell.

The amateur will (very often) be interested in Anode wear rate, whether or not the power supply to hand is suitable or how much product will be produced per week.

The amateur will be using (probably) a non pH controlled cell, this is OK. All industrial setup's use pH control.

The amateur will probably use what is to hand which may be a cheap power supply, cheap Gouging rods etc. The cell container can come in the form of a bucket with a lid. The plastic that the bucket is made from must be able to withstand the cell electrolytes and fumes. A PVC bucket is ideal. Some holes are drilled in the lid to accommodate the electrodes and a vent tube. The vent tube is useful as it allows gasses to be vented out of the building in a controlled manner. A hole about 5cm in diameter is also made in the lid for looking into the cell and also for adding water or NaCl solution as required. A piece of plastic is needed for to cover this hole and stop fumes and mist from getting out of the cell onto connections etc. A stainless steel or even mild steel bucket can be used. This can then be used as the Cathode thus doing two jobs at the same time. Remove solution from container when current is stopped or it will corrode.
The electrodes should be sealed into the lid because if fumes and mist are getting on connections you will have problems trying to maintain them. Also gases coming to the surface of the solution generate a mist of the solution which will drift out of the cell. This mist will rust everything in the vicinity of the cell and beyond!.

The design parameter that always raises it's head is the Anode current density. This parameter is important because you must keep below a certain Anode current density to avoid eroding the Anode. This is particularly true with Graphite. Anode current density is the Anode current (cell current) divided by the total surface area of the Anode which is in the electrolyte. It is usually quoted in Amps per square cm. When you have decided what the Anode surface area will be and what the current density on the Anode will be, you will know what the maximum current through your cell can be. You do not have to run this maximum, you can run less current into the cell if you so wish.

Another design parameter that gets discussed is the ratio of the size of the cell (the liquid volume) to the current going into the cell. This in not a critical parameter. It has little effect on current efficiency. When the current going into the cell is raised (if you add more Anodes say and adjust power supply) and the cell volume is kept constant in order to shorten the run time of the cell, there will come a point where the heat generated by the process will not be able to escape fast enough from the cell and the temperature of the cell will be too high. If you must run a large current into a small volume of electrolyte you can keep the cell cool by putting it into a large container of water. Industrial setup's uses cells that are small in relation to the current going into them. They use cooling coils in the cells to keep the cell cool and transport heat away. This keeps the real estate used by the cells small. The amateurs cells can be large in comparison to the current going into them. The only disadvantage in doing this is that the run times of the cells can be long. This can leave the impatient amateur feeling as if nothing is happening at all as he is forced to wait perhaps two weeks before he can take out a crop of Chlorate. The cells WILL still be making Chlorate at the same rate as a smaller cell with the same current going into it.

The amateur very often comes up with some electrode arrangements for to stop Chlorine gas from escaping from the cell. It should be noted in industry that most cells use a very simple arrangement of parallel plates in a vertical arrangement. With the amateur cell the pH is not controlled. It is next to impossible for Chlorine gas to escape out of a cell which has a high pH (amateur cell). There will be a smell of Chlorine at the start but once the pH rises no Chlorine of any significance will come out of the cell. Add NaOH or KOH at start if there is a problem regarding smell of Cl2.

The temperature of the cell (IMHO) is of little importance in non pH controlled set up. All Chlorate is made by electricity (not by species meeting in the bulk of the electrolyte as you have in pH controlled setup's) with little or no bulk chemical reactions going on. Temperature should be kept at a level so that Anodes are not damaged/eroded. Very low temperatures may cause Na or K Chloride to come out of solution.

The power supply for to supply the cell with this current will ideally be a controlled current source. With a controlled current source you set the power supply to put a certain current into the cell and the voltage across the cell will vary as the cell resistance varies.
Most power supplies for sale or to hand are NOT controlled current sources. They are controlled voltage sources (either fixed or variable).
This means that when you connect the supply to the cell the voltage across the cell in rock steady at whatever the voltage of the supply is set at (assuming the supply is not being abused) and the current put into the cell is dictated by that (rock steady) voltage and the resistance of the cell. If the supply has a variable voltage output then the current can be varied by lowering or raising the voltage of the supply.
When the power supply is a fixed voltage output (you cannot vary the Voltage with

a knob. An example is a computer power supply) then the only way you can vary the current is by manipulating the electrodes in the cell or you could add a resistor or a number of diodes in series with the line going into the cell to lower the current. With a computer supply (5 Volts output) the current going into the cell will probably be within acceptable limits. If you have a fixed 10 or 12 volt supply then the current will probably be excessive and you will need a resistor or diodes to limit current. Another trick is to put two cells in series so that less current will flow into each cell. Make sure the cells share the current sensibly. Diodes work by dropping 0.9 Volts across themselves, they effectively lower the power supply voltage seen by the cell by 0.9 Volts.
12 Volt battery chargers can make an acceptable supply as they tend to have controlled current characteristics. They are a half way house between a controlled current source and a controlled voltage source.
You will need a current meter in the line going into your cell (or in the power supply itself) in order to measure current. Voltage across cell can also be noted.

Do not get obsessed with the voltage across the cell. The voltage across the cell will have a value no dough. Some are inclined to latch onto the voltage appearing across the cell as if it were some very important, almost magical, parameter. Some times you will hear a statement like: "I ran my cell at 3.6 volts, therefore I was making Chlorate. I increased the voltage to 7.4 volts and I am now making Perchlorate". It is NOT the Voltage across the cell that decides if you are making Chlorate or Perchlorate. If the Voltage is too low not enough current will get pumped into the cell. This will give you slow production. If you have a bad connection which causes a large Voltage drop this will lower current going into the cell too. Think in terms of Anode current density.

Cathodes

Titanium is King when it comes to cathodes. It is relatively expensive. Stainless steels are next best but be aware that if they corrode (as when you do not have the cell in operation perhaps) they will release Chromium into your cell which is not wanted when using Lead Dioxide anodes. The Anode should have a cathode on each side (surrounded). It is not a critical design factor, keep it sensible.

See Wouters page for more information on cell design.

Some cell design examples

Example 1

The designer has decided that he wants to make 1Kg of Sodium Chlorate per week. he is not too strapped for cash.

How much Anode surface area needed:

He has no Anode(s) or no power supply yet. By looking at the run times section for Sodium Chlorate on this page the following fact is noted. In a typical Amateur cell you will get 0.00596 grams Chlorate formed per minute per Amp. That’s the same as 60.0768 grams formed per week per amp (There are 10,080 minutes in a week) Therefore to make 1000 Grams per week you will need to run 1000/60.0768 = 16.64 Amps (say 17). Looking at the max. allowable current densities on the different Anode materials will give figures similar(ish) to theses: Platinum 300mA/square cm, Graphite 30mA/square cm, Lead Dioxide 300mA/square cm, and Magnetite 30mA/square cm. He may like to run his Pt, LD, or Magnetite Anodes at a higher current density as the figures above are fairly conservative. He will not want to run his Graphite Anode at a higher current density so as to keep erosion at bay. Having decided what Anode material he is going to use he then sets about deciding how much surface area he needs on the Anode. Assuming Graphite, he will need 17/.03 = 566 square cm Min. That’s the Anode surface area that is immersed in the electrolyte remember. He then decides if he is going to use Gouging rods, EDM Graphite or some other Graphite. He may wish to use the Graphite at a much lower Anode current density to keep Anode erosion ever lower. If he wishes to halve current density, he will do so my simply doubling the Anode surface area. If using rod shaped electrodes be advised that as the rod wears it will have a smaller surface area, the current density will rise (assuming current into cell remains the same) and wear rate will increase. It may be advisable to start with a low current density so that as the Anode wears the current density will not go above 30mA per square cm. If using flat pieces of Graphite the Anode wear will not have much effect on the surface area of Anode.

How much NaCl:

In order to make 1Kg of Chlorate you need exactly (1000 X 0.55) grams of NaCl. The 0.55 comes from the division of the molecular weights. The electrolytic cell and the Anode will not operate under such clear cut conditions. You will need at least 100 grams per litre NaCl to be left in the cell after your run so that the conditions for Graphite Anode erosion are met. If you try to use up all the Chloride the Anode will get eaten away rapidly coming toward the end of the run. So: We need to use at least 550 grams of salt for to be converted to Chlorate + 100 grams per litre to be left in the cell at the end of the run. He will need a container that will hold approx. 3 litres of solution. This is a minimum size. If you run 17 amps into this 3 litre container you will have problems keeping it cool. Better to just use a container that is much much bigger than this. About 25 litres would be great filled with saturated NaCl solution. This will stay cool. About 330 grams NaCl will dissolve in 1 litre of water. At 17 amps you will still get the same amount of product forming (assuming similar current efficiency which is probable). It may not suit the impatient amateur as he will not be able to draw product from this larger container until a few weeks have passed. He may add Chromate, Persulphate or NaF to increase current efficiency. He will add water to the cell to keep volume steady. He may add salt solution. If he adds salt solution he needs to factor this into the run time.

Power supply:

He will probably purchase his power supply. The exact output voltage of the power supply needed to drive 17 amps into the cell is unknown. It will be somewhere between 3 and 6 volts. He will probably purchase a DC power supply having the ability to supply at least 17 amps at a fixed voltage anywhere between 1 and 10 volts. The power supply will have a nice current meter to tell him what amps are going into his cell. It will also have (though not essential) a nice volt meter to tell him what voltage is across his cell. He will be careful that he does not become too obsessed with the voltage across the cell. The current going into the cell may vary a small amount as the cell runs. The temperature, ageing of Anodes and changing concentrations of salts will vary the resistance of the cell somewhat. He may have to adjust the voltage a bit to keep current at exactly 17 amps. He may choose not to worry about the fact that the current is not staying at exactly 17 amps.
If he is very dedicated to Chlorate making he will purchase a power supply that has

the ability to put a programmed current (a power supply which is a fixed current source) into his cell. He will set the supply to put 17 amps into his cell. There will be a meter for measuring current and (for interest) a meter to measure the voltage across the cell. The current going into the cell will remain rock steady at 17 amps, the voltage across the cell may vary a bit as the resistance of the cell varies.

Cathodes:

He will choose cathodes that will be at least similar surface area to the Anode(s) and place them around the Anode(s) in a sensible fashion. It is wise to place cathodes each side of Graphite Anodes in order to keep the current distribution on the Anode surface fairly even. If he were to place the Cathodes at one end of the cell, the current density on the side of the Anodes closest to the Cathodes will likely have a greater value than the side that is not toward the Cathodes which will have consequences for erosion, especially with Graphite.

Example 2

The Amateur has a computer power supply and he is thinking of purchasing some Gouging rods from EBAY and he wants to make as much Chlorate as he possibly can. He is rather strapped for cash. He has a multimeter.

How much Anode surface area needed:

Firstly test supply with a resistor to see if it is working. We have a power supply that puts out a fixed voltage of 5 volts DC and a few other voltage outputs (12V and others). **We use the 5 volt output which is the main output**. The supply also has a maximum current output on this 5 volt output which is hopefully stated on the supply. The maximum current that this line can supply is the maximum current you can put into you cell without risking damage to the supply. **Calculate the Anode surface area from this maximum available current**. Say the maximum current is 10 amps this means that you need at least an Anode surface area in the electrolyte **of 10/.03 = 334 square cm.** (This comes from the fact that you want to keep the Anode current density below **30mA per square cm to keep Graphite erosion at**

bay). How many Gouging rods do you need to give you this surface area? The area of a rod is (ignoring the small circle at the bottom of the rod) Pi X Dia. X h (remember h is the length of rod actually in the electrolyte). Use at least this amount of rods. It would be great to use twice as many to keep Anode current density real low and therefore keep erosion low. This is especially true as the Gouging rods wear, their surface area will decrease, current density will increase and erosion will increase.

How much NaCl:

Use a container that is about 10 litres or larger in size filled with saturated NaCl solution. About 330 grams NaCl will dissolve in 1 litre of water. Use a 20 (or a 30!!) litre container if you like. Calculate the run time and keep in mind that you must stop running the cell when you have got to the stage where you have 100 grams per litre Chloride so as to keep erosion on the Graphite to a sensible limit. He may add Chromate, Persulphate or NaF to increase current efficiency>

Cathodes:

He will choose cathodes that will be at least similar surface area to the Anode(s) and place them around the Anode(s) in a sensible fashion. It is wise to place cathodes each side of Graphite Anodes in order to keep the current distribution on the Anode surface fairly even. If he were to place the Cathodes at one end of the cell, the current density on the side of the Anodes closest to the Cathodes will likely have a greater value than the side that is not toward the Cathodes which will have consequences for erosion, especially with Graphite.

Running the cell:

The supply is connected and the voltage and current is measured. The voltage across the supply is measure to see that it is not being abused, ie. too much current being drawn from it. The current will be measured to ascertain how much product you will be making per week. Measure the voltage across the cell. If the voltage is below 5 volts the cell is drawing too much current and the supply is in danger of burning out. Measure the current to see what it is. Be sure that the multimeter will take the current that may be flowing. It may be lower that the supply rated current as the supply may have heated up so much that the thermal shutdown in the supply

has come into play. You can put the Anodes and Cathodes further apart or put diode(s) in series with the line going into the cell in order to raise the resistance seen by the supply (this will lower the current below the maximum that the supply can handle). Run the set-up so that the current is below the maximum (say 10% below) allowable for the supply. You will have 5 volts across the supply terminals at this point because the supply is a fixed voltage type of supply that was made to supply current at a fixed five volts. If you have used diode(s) to manipulate the current through the cell, the voltage across the cell will be less that the voltage across the supply by (0.9 X [number of diodes]) volts.
The amount of Chlorate you will be making will be:
60.0768 grams per week per amp, 9 amps will give you 540 grams per week. (assuming around 50% current efficiency. You will not be able to crop this amount in the first week. It depends how much electrolyte you have started off with. You need to run the cell for the amount of time as described elsewhere on this page. He will add water or salt solution to the cell to keep the volume constant. If he uses salt solution he will need to factor this into the run time. Be patient.

Example 3
The designer has a Lead Dioxide Anode and a huge 12 Volt battery charger. He is not to concerned with making the maximum Chlorate possible per week but he is very impatient and wants Chlorate NOW.

How much Anode surface area has the Anode:

The amount of the Anode that will actually be in the electrolyte is used to calculate the surface area of the Anode. A current density of 300mA per square cm is easily accommodated with a Lead Dioxide Anode. He may wish to run his Anode at a smaller current if he so wishes but since he is impatient for product he may decide to run the Anode at a higher current density. Assuming the area of the Anode is 70 square cm, this will allow a current of 70 X 0.300 = 21 Amps to be run though cell.

How much NaCl:

The cell volume will be kept small so that Chlorate can be extracted as soon as possible. Looking at run times described elsewhere on this page he sees that with

21 amps running into the cell will give him about 21 X 0.00596 = 0.12516 grams Chlorate formed per minute, which is 180 grams per day. He will set up his cell so that he can extract Chlorate after two days, ie. 360 grams theoretical. In order to make 360 grams Chlorate, 360 X 0.55 = 198 grams Chloride are needed. Since Lead Dioxide does not get eroded by low Chloride concentration there is no need to have a quantity of 'buffer' Chloride in the cell as far as Anode erosion is concerned. It will be impossible to convert all of the 198 grams of salt into 360 grams Chlorate as run times are (as described elsewhere) based on having a decent amount of Chloride in the cell at the end of each run. He will use 270 grams NaCl dissolved in somewhat less than one litre of water. Also if he uses too little Chloride he may get Perchlorate forming if the concentration of Chloride falls below (approx.) 10 grams per litre. He may add NaF or Persulphate but not Chromate to increase current efficiency.

Cathodes:

He will choose cathodes that will be at least similar surface area to the Anode and place them around the Anode in a sensible fashion. It is wise to place Cathodes each side of the Anode in order to keep the current distribution on the Anode surface fairly even. If he were to place the Cathodes at one end of the cell, the current density on the side of the Anode closest to the Cathodes will likely have a greater value than the side that is not toward the Cathodes which will probably have consequences for erosion. Lead Dioxide is fairly robust though.

Running the cell:

The cell is less than one litre is size and has 21 Amps going into it. This cell will heat up too much. The cell can be placed sitting in a large container of water so as to keep it cool. The power supply will be set up to run 21 amps through the cell. The open circuit voltage of the (big) battery charger will be approx. 13 volts. When connected to the cell it will probably send too much (more that 21 amps) into the cell. The current going into the cell can be decreased by adding a resistor or diodes in series with the input of the cell. The voltage across the cell will be in the region of 4 to 6.5 Volts (approx.) The voltage across the charger will be 12 volts nominal. The current going into the cell will not be a perfect smoothed DC but this is not a problem. It will be difficult to measure the exact effective current because of this. There will probably be a current meter on the charger which will give an accurate

enough indication of the current. If a battery of reasonable quality is connected to the charger it will act a a huge capacitor and the set up will have a nice steady current (and Voltage) going into the cell. If no battery is available it is OK. The cell will be run for 2 days and the Chlorate extracted by evaporating some of the water away and letting it crystallize out. If he does not turn of the power after 3 days he may get Perchlorate starting to form.
After a crop or two of Chlorate he may decide to be more patient regarding the process, use a much larger container and allow Chlorate to accumulate before extraction. He will add water to the cell to keep volume steady. He will not add salt solution since he want Chlorate quickly.

Example 4
The designer has a bench power supply with a maximum output current of 3 amps. He is going to purchase some Platinum wire or a Platinum clad Anode. Cash is scarce.

How much Anode surface area should he purchase:

This is entirely up to himself. He will look at the price of the wire and weep. If he wants to run the set-up at the max. current that his supply can give (looking at typical current densities used for Pt. of 300mA per square cm) he will need 3 amps/0.300 amps = 10 square cm of Platinum in the electrolyte. He will purchase Pt wire with a sensible diameter which will carry 3 amps. If he purchases Pt. of (say) A.W.G.(B & S) = 42 (that’s S.W.G. between 45 & 46) this will have a diameter of 2.5 thousands of an inch. This measly wire will not carry 3 amps. It will melt. He will purchase wire of approx. 25 A.W.G (26-27 S.W.G) which will carry 3 amps. This wire is still thin, around 19 A.W.G. would be nice so that the Anode will be self supporting.
The surface area of a cylinder is D X Pie X L. Assuming we use 19 A.W.G. (D = 0.9119mm) we need a length of wire which is 10/(3.142 X 0.09119) = 35 cm. He will need another inch to come up out of the cell, say 38 cm total length. He will bend the wire into a shape for to use as the Anode. Some like to wind the wire onto a former (say a glass tube). Winding the wire onto a tube will have some consequences for current distribution on the Anode. The Anode will have a very small current density on the wire next to the

tube, it will have a larger current density on the side of the wire away from the tube. Keep this in mind. It would be good to wind the wire in a spiral of about 2 inches Dia. that is self supporting.

The price of this Anode will not be small. The smaller the Dia. of the wire you use the less Dollars you need to spend to get a certain surface area. See the section on the Pt. Anode. You could buy half the length suggested and squeeze (run through a mandrill) or hammer the wire so that it's surface area is doubled (or more) thus saving Dollars.

If he uses a Platinum clad Anode all his current carrying problems will end as the substrate of the Anode will carry 3 amps easily. He still needs 10 cm squared of Anode area in the electrolyte.

Since the Anode is so expensive he may decide to purchase less surface area and run the Anode at a higher current density, still running 3 amps into cell. Pt. will take quite a high current density without eroding. He could also purchase light wire that will not carry 3 amps but will carry (say) 0.5 amps. He will cut this wire into 6 equal lengths and have 6 Anodes coming out of the cell connected to a bus bar (like a comb arrangement). Anode surface area in the electrolyte must still be 10 square cm to give similar erosion conditions to the single Anode. The 6 Anodes will save cash and give him more work.

How much NaCl:

Looking at the run time section elsewhere on this page it is noted that 3 amps will give you (0.00596 X 3) = 0.01788 grams Chlorate formed per minute = 180.25 grams per week (current efficiency about 50%). This will use 180.25 X 0.55 = 100 grams Chloride per week. The 0.55 comes from division of the molecular weights of NaCl and Na Chlorate. Assuming that he wants to harvest Chlorate once per week he will need 100 grams Chloride in solution + (about) 100 grams Chloride per litre left at the end of the run so that erosion of the Anode is kept at bay and to keep current efficiency at a sensible level. Platinum will erode somewhat if used in a cell that has a low Chloride concentration in it. About 330 grams NaCl will dissolve in 1 litre of water. He will dissolve approx. 145 grams NaCl in about 0.45 litres water. After a week approx. 40 grams of Chloride will be left per 100ml solution. He will stop his cell at that point so that erosion of the Anode is kept at bay. He will add NaF, Chromate or Persulphate to increase current efficiency. He may decide to top up the cell with water or salt solution. If he used salt solution he must factor this into the run time.

Cathodes:

He will choose cathodes that will be at least similar surface area to the Anode(s) and place them around the Anode(s) in a sensible fashion. It is wise to place cathodes on all sides of Anodes in order to keep the current distribution on the Anode surface fairly even. If he were to place the Cathodes at one end of the cell, the current density on the side of the Anodes closest to the Cathodes will likely have a greater value than the side that is not toward the Cathodes which will have consequences for erosion. If he has a spiral type Anode he will place a rod inside the coil and a few (3 perhaps) around the outside of the coil. If he has a flat Platinised Anode he will place a sheet each side of the Anode.

Running the cell:

He connects his bench power supply up to the cell. + to Anode, - to Cathode. He increases the voltage until He gets 3 amps to flow. He will keep an eye on the current so that it does not increase above 3 amps and abuse the power supply. The current will vary somewhat as the resistance of the cell varies due to temperature and solute concentration changes. The voltage will be in the region of 3 to 6 volts. He may wish to connect a high wattage resistor in series with the power supply and increase the voltage of his power supply so that the current flowing will not be so dependent on the whims of the cell. Doing this will not increase the voltage across the cell. If he uses a 1 ohm resistor (with at least 3 watts dissipation ability) and increases the voltage of his power supply by 3 volts the current will still be 3 amps. As the resistance of the cell varies the current will not vary quite so much, as the added resistor 'swamps' or helps to mask the effects of changing cell resistance. The supply (now consisting of a voltage supply + a resistor) has some characteristics of a controlled current source. If he is not too worried about the current varying a little bit (or he doesn't’t know/care what the heck I am talking about) then he can leave the resistor out.

Practical run time calculation

The formula gives the run time's for your Sodium Chlorate cell, based on the number of amps and the total amount of Chloride that you have added to the cell. 54% current efficiency is the approx. conversion efficiency that you will get with a non pH controlled cell when the Sodium Chloride concentration is not below about

100g/l. When this run time is used you will not get all of the Chloride converted into Chlorate. The time is calculated such that there will be about 100g/l of salt left in the electrolyte when the run is complete.
This is what we want because at about 100g/l of NaCl the current efficiency starts to get effected due to low Chloride concentration (pH control or not) and is considered too low to tolerate. The total amount of salt in the cell minus the 100 grams per liter that we are not going to convert is called the *'available Chloride'*.

If you are getting higher current efficiency from your set up **(say you are controlling pH)** then you will have shorter run times. With good pH control you can expect 80% or more current efficiency.

If you are using salt solution (recommended if you are going to take out a crop of solid chlorate) to top up your electrolyte, it simply means that you will have to recalculate your run time each time you add some solution taking into account the extra salt that you have added to the cell. If the cell has a lid this will not be realizable as there will not be any evaporation.

A quick way to calculate run time is to note how many moles (58.5 grams) of *'available Chloride'* there is in the cell. It will take 12 moles of electricity (321.6 Amper Hours) per mole (58.5 grams) of *'available Chloride'* to finish the cell. [This is at 50% current efficiency and leaving 100g/l of Chloride in the cell at the end of the run.]

Figure in minutes(decimal) per ('available')gram NaCl for different current efficiency's

Amps	40% Current efficiency	54% current efficiency	60% current efficiency	80% current efficiency
2	206.25	152.70	137.43	103.07
4	103.07	76.35	68.72	51.54
8	51.54	38.16	34.36	25.77
10	41.23	30.54	27.48	20.61

15	27.49	20.36	18.32	13.74
20	20.61	15.27	13.74	10.31
30	13.74	10.18	9.16	6.87
50	8.25	6.12	5.50	4.12
75	5.50	4.07	3.66	2.75
100	4.12	3.05	2.75	2.06
150	2.75	2.04	1.83	1.374
200	2.06	1.53	1.37	1.031

It can be illuminating to know how much Chlorate you are getting per minute of operation of your cell. If you are getting 54% current efficiency you will get 1 gram of Sodium Chlorate per amp going into your cell every 167.76 minutes, or if you like, 0.00596 grams Chlorate formed per minute per amp.
So if you are running your cell at 10 amps you will get 10 grams Sodium Chlorate every 167.76 minutes, or 0.0596 grams per minute. At 100 amps you will get 0.596 grams per minute of Chlorate forming, that's 858 grams per day.

The following is a useful little program for calculating run times for cells and also will tell you at the press of a button what amounts of Chlorate to expect from your cell in a given time.
Chlorate cell calculation program (106K).
It is not a good idea to download programs from the INTERNET "willy nilly" and run them, as they may contain viruses

Reaction equations and cell chemistry

Some Relevant species	
Dichlorine Oxide	Cl2O
Chlorine Dioxide	ClO2
Chlorine Trioxide	ClO3
Dichlorine Heptoxide	Cl2O7
Hydrochloric acid	HCl
Hypochlorous acid	HClO
Hypochlorous ion	ClO^-
Chlorous acid	HClO2
Chloric acid	HClO3
Perchloric acid	HClO4
Sodium salts	
Sodium Chloride	NaCl
Sodium Hypochlorite	NaClO
Sodium Chlorite	NaClO2
Sodium Chlorate	NaClO3
Sodium Perchlorate	NaClO4

There is not much to be said here that has not been said elsewhere. The reactions that occur inside a Chlorate cell are not easy explained by the non-professional to the non-professional. What actually happens, how fast it happens and what way it happens depends on a lot of factors including: pH of bulk solution, temperature, concentration of starting, intermediate and end products, stirring of cell contents, current density on electrodes and current concentration in the cell, additives in cell, ratio of total volume of cell to area of electrodes, spacing and arrangement of electrodes, type of electrodes, cell voltage...and more.
To complicate matters more the effects of each of the parameters cannot be studied in isolation as all the parameters interact with one another in a complicated way. You also have the added complication of how YOU would like your system to behave. The industrial manufacturer will be very concerned with power consumption. The amateur will not be very concerned.
All theses factors create a lot of healthy debate.

It should be noted that the Non-Professional cell will probably be operated at a high pH (ie. no pH control). When this is the case, practically all of the Chlorate is made by electricity and therefor there will be no chemical conversion of intermediates into Chlorate in the bulk of the solution, and therefor the temperature of the bulk solution will be somewhat irrelevant. Also the maximum possible current efficiency in this situation is 66.7%
If pH control is to be realised, you will have to set up a system to drop HCl into the cell continuously. Throwing a 'slash' of 10 or 20% HCl into the cell every half day or so is not sufficient.

The diagrams below attempts to show the overall reaction in a simplified manner
See What is a mole if you don't know what a mole of a substance is.

There is a good discussion of Chlorate cell chemistry in the 'Further Reading Section' , Ullman. Chlorine Oxygen acids and Salts. See also
Comprehensive Treatise of Electro chemistry Vol. 2 Electrochemical Processing. J. O. M. Bockris, B. E. Conway, E. Yeager, R. E. White. Plenum Press, N.Y. 1981, also The Kirk-Othmer Encyclopedia of Chemical Tech.

The diagram on right shows the dependency of the concentration of intermediate species in the chlorate cell on pH. At a low pH the cell will generate chlorine gas which will escape out of the cell which will cause the pH to rise up. As the pH rises the ease with which chlorine can escape out of the cell gets less and less and the cell will stabilize at a pH of about 9 or 10. It will depend on the design of your cell. At this pH practically all Chlorate is made by electricity at a maximum possible current efficiency of 66.7%.

Additives are added to Chlorate cells (and Perchlorate cells) in order to eliminate reduction at the Cathode. At the Cathode, Chlorate and Hypochlorite are reduced which is undesirable. Adding Fluoride, Persulphate, or Chromate (and others) help to eliminate this problem. It should be noted that Chromate's are not suitable for use with Lead Dioxide as they interfere with it's operation.

Controlling the pH

The pH of the cell increases if you do not add acid to the cell. This is caused by Chlorine gas escaping from the cell. As the pH rises up to about 9 or 10 the Chlorine is no longer able to escape and the pH will stabilize.
If you want you can control the pH of your cell. This will dramatically increase current efficiency and also give less erosion if you are using Graphite anodes. There is little point in throwing in a 'slash' of acid (say) twice a day in a effort to control pH. You will have to set up a system to drop dilute HCl into the cell. I have heard that 1% solutions are used in industry, but you could probably use stronger. pH stats are used by industry. **The cell chemistry changes dramatically when the pH is held at the optimum and the optimum cell design changes too.** When you are controlling pH it is good to have a fairly large bulk of solution in your cell so that there is plenty of space away from the anode for the bulk reactions to take place. Industrial set up often have two parts to a Chlorate cell. The

first part has the electrodes closely arranged so that the solution spends minimal time between the electrodes. The solution (now rich in intermediates) flows into a bigger tank where bulk reactions take place.
When the cell is pH controlled the current efficiency goes up as temperature goes up. As a rough figure you can expect a 6% increase in current efficiency as you increase the temperature of your cell from 30 to 80C.

If you are not controlling pH there is little point in having conditions favorable to bulk reactions IMHO. Most of the Chlorate will be made by electricity alone, therefor temperature will not have much effect on current efficiency. Note that Magnetite anodes will not make Chlorate at sensible CE if there is no pH control.

There will be a smell of Chlorine gas as soon as the cell run is started. As the pH rises the Chlorine will be unable to escape from the cell which will happen fairly quickly. If the smell of Chlorine in a problem at the start you could raise the pH immediately be adding some Na or KOH.

This table shows the effect of pH control on current efficiency and acid consumption

Quality of pH control	pH drift	Current efficiency, %	35% HCl consumed kg/ton - $NaClO_3$
Medium	6.0 to 7.8	74.4	87.5
Good	6.7 to 6.8	84.5	62.5

From: Electrochemical Technology. 6 (1968) 402. Magnetite anode was used.

As can be seen from the above diagrams and tables, **it is very beneficial to operate a pH controlled cell at a high temperature (assuming it will not erode the anode).** Not alone does this increase current efficiency directly (by helping the bulk reaction take place) but it also lowers the amount of acid required to produce a given amount of Chlorate. It is also beneficial to control the pH accurately. This increases current efficiency directly and it also decreases the total acid requirement for a given amount of Chlorate produced.

The acid requirement for a given amount of Chlorate produced will go down as current efficiency goes up.

With the pH of the cell at the optimum, the quantity of Chlorine escaping from the cell will be greater than a similar cell run at a pH of ~9 (pH not controlled). This represents a current loss (ie. some current is wasted producing Chlorine for no good reason). It also represents a molar loss. The extra amount of Chlorine escaping from the cell is very small as can be seen from the graph.

Removal of Sodium Chlorate

When it comes to getting a crop of Sodium Chlorate out of the cell you should aim to have at least 600g/l of dissolved Chlorate in your electrolyte. This concentration of Chlorate together with the NaCl will cause a crop of Na Chlorate to ppt out of the electrolyte when it is cooled to zero and below.

You will not get very much though, in fact you will not be able to get any the first time you run your cells without boiling off some water. The problem is that on the first run of your Chlorate cell the concentration of Sodium Chlorate will not be very high and you will not get a ppt of Chlorate, it will stay in solution.

There are several approaches you can take. You can simply carry on adding more Chloride and run the cell more so that the concentration of Chlorate will go on rising and eventually you will get a sensible crop of Chlorate from the cell by cooling. You need evaporation to happen so that there is room for continuous top up. If running a cell which has a lid on it this is not possible. You can also boil off about half of the solution volume so that the concentration of Chlorate will be doubled and you will now get a sensible crop of Chlorate by cooling. See below for an explanation of what is happening.

The diagram below is the same as the one above but the scales are now equal on both axis. It is more illuminating IMHO.

When you start off your cell for the first time you will be at point X on the graph. If you do not add any Chloride solution to your cell and you run your cell for the recommended amount of time given by the run time formula, you will be left with about 10g/l00ml (100g/l) of Chloride in the cell and the rest of the Chloride (25g/100ml) will have been converted into 106.5/58.5 * 25g = 45.5g Chlorate per 100ml solution. This in point Y on the graph. As you can see you will not get any Chlorate out by cooling. If you boil off about half of the solution volume you will get to point Z on the graph (some Chlorate may come out of solution before you actually get to point Z). If you now cool your solution to Zero (that’s point M) you will get about 43 grams of Chlorate per 100ml of solution to come out of solution.

Say you have been adding Chloride solution to your cell as it was electrolysing, and that you added a total of 20 grams Chloride per 100ml solution to your cell. Assuming that you ran your cell for the amount of time as given by the run time formula you will have left in your cell 10 grams (per 100ml solution) of Chloride not converted to Chlorate. In other words you will have converted 35 + 20 - 10 = 45 grams (per 100ml solution) of Chloride into Chlorate. That’s 106.5/58.5 * 45 = 82 grams Chlorate per 100ml of solution. That’s about point A on the graph. If you cool your solution to zero (or below) you will get about 26 grams Chlorate per 100ml of solution to ppt out of solution (or more if you go below zero). If you boil off some of the solution volume before you cool you will get even more. It is up to you to figure out what exactly you want to do. Remember that if you do not take out the Chlorate this time around you will get it out the next time you harvest Chlorate after another cell run as the Chlorate concentration will be higher.

Another good way to get Sodium Chlorate out of the solution it to add some concentrated NaCl to the solution. This is called 'salting out' in the industry. The solubility of the Chlorate decreases markedly as the Chloride concentration goes up. See the mutual solubility graphs. The NaCl will be used when you start running the cell again. Take a note of the amount of Chloride that you added. You can lower the temperature of your electrolyte to -20C to get out a bigger crop of chlorate also. I do not know anything about salting out.
Note that Aluminium containers are not suitable for boiling the Chlorate solution in, as it will blacken the produce with corrosion products.
The solid Chlorate can be washed with very cold water (and recrystallized, but there is no need) and put into the Perchlorate cell. It will not matter if there is a small amount of NaCl contaminant in the Chlorate because the Perchlorate cell actually causes the Chlorate ion to dissociate and a small amount of Chloride is actually formed in the Perchlorate cell.(J. C. Schumacher, The Perchlorates. Page 84)

When your chlorate cell is stopped running it will have a quantity of Hypochlorite (an intermediate product) in it. It is recommended that this hypochlorite be destroyed before going on to recover your solid Na Chlorate or make K Chlorate. This can be done by boiling your solution for about 15 minutes (you may have to do this anyways to concentrate the solution if you are separating out solid Sodium Chlorate) or by adding about 1g urea per litre of solution. It is difficult to get rid of the hypochlorite by boiling alone. I don't know what are the disadvantages of Hypochlorite in the Chlorate. It won't matter very much if you are going on to make Perchlorate as it will eventually all be destroyed in the Perchlorate cell.

The cell liquor (mother liquor as it is called in industry) will now be returned to the Chlorate cell. It is difficult to give a figure of how much Chloride and Chlorate will be in the mother liquor. It depends of how much Chloride you put into the cell, how long it was run, the current efficiency and how much Chlorate was extracted. If you used the practical run time calculation above there will have been about 100g/l NaCl unconverted to Chlorate in the mother liquor when it came out of the cell. Dry the extracted Chlorate and weigh, this will also give you an idea but remember that there will be quite a lot of Chlorate 'stolen' from your expected yield (especially on the first extraction of Chlorate from a new cell) as it is very soluble. If you used 'salting out' to get a bigger crop of Chlorate crystals you must (obviously) take the amount of Chloride you added into consideration, in fact you can add the appropriate amount of Chloride for the next run at the 'salting out' stage and have done with it.

It should be noted that Sodium Chlorate is very soluble and you may be disappointed with the yield of Sodium Chlorate that is obtained when you take product from your cells for the very first time. There will be large amounts of Sodium Chlorate still dissolved in the mother liquor and when this is recycled into the cells you will get a much bigger yield of Sodium Chlorate in subsequent runs of the cell. If you have not been topping up your cells with Sodium Chloride when they were running for the very first time you wont be able to get any! Chlorate to come out of solution by cooling alone, you will have to boil off about half the volume of the solution in order to get Chlorate to ppt out. In subsequent runs (assuming you recycled your mother liquor into the cells) the Sodium Chlorate concentration will be much higher and it will ppt out more easily. You may still wish to boil off some water as described above.

A diagram showning mutual solubility in Kgs is below.

Removal of additives

If Chromates have been added to you cell for efficiency reasons or to protect Iron or Steel Cathodes then it should be removed. Chromates can be removed from the cell by adding the correct quantity of Barium Chloride. The Chromates will be precipitated out as insoluble Barium Chromate.

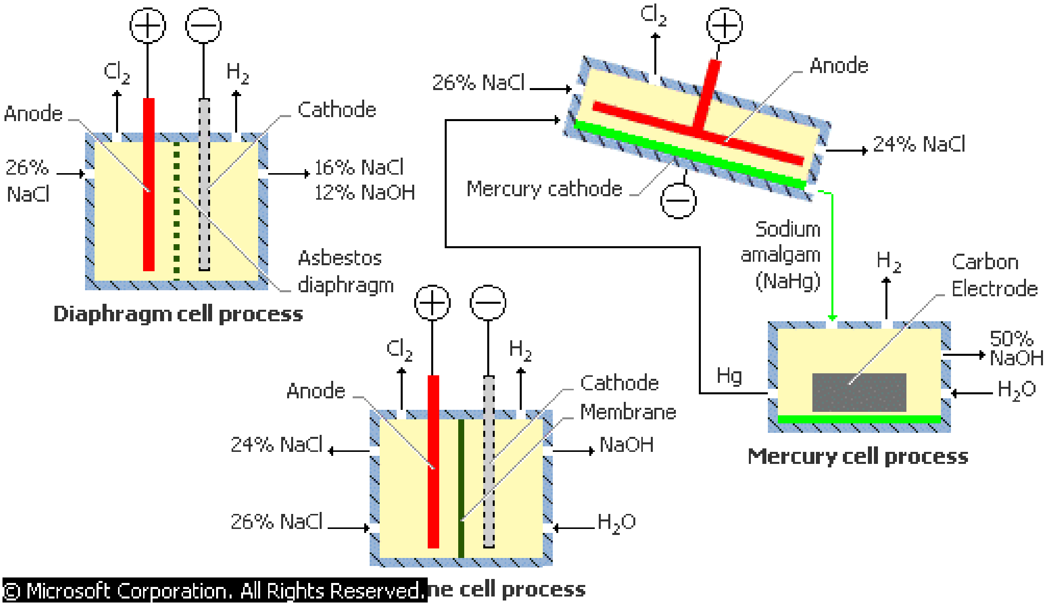
I do not know how to remove Persulphates or Flourides from the electyrolyte nor do I know what effect small amounts of Persulphates or Flourides will have on pyrotechnic compositions.

Be patient

The single most important thing about making Chlorates or Perchlorates **is patience. Run-times tend to be 1-2 weeks**, as cells with passive cooling can't take much more than 1-2 Amp per 100 ml. Purification of Potassium Perchlorate will take *at least* three crystallisation cycles to achive a purity sufficient for good pyrotechnic blues. This takes several days of part-time work as you can only do 1-2 cycles a day because of the cooling time. This also involves a large volume of water and evaporating the supernatant liquid to recycle what is dissolved in it will take an hour or two per cycle.

pH control isn't a big deal

You will get more efficiency benefit for less engineering hassles by keeping the Chloride concentration up than maintaining the pH precisely. To do pH control properly you will need a closed-loop system, you can't just add some HCl each day or rely on a syringe pump or similar metered dosage system. The pH will stabilize fairly alkaline and the efficiency remain better than 50% as long as the Chloride concentration is kept above 300 g/l.


Cl$_2$
H$_2$
Anode
Cathode
26% NaCl
16% NaCl 12% NaOH
Asbestos diaphragm
Diaphragm cell process
Cl$_2$
26% NaCl
Anode
24% NaCl
Mercury cathode
Sodium amalgam (NaHg)
H$_2$
Carbon Electrode
50% NaOH
H$_2$O
Hg
Mercury cell process
Cl$_2$
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24% NaCl
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