Practical guide to chlorate and perchlorate electrolysis

Laboratory guide of informative and technical nature.

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Summary

1 - Electrolysis principle :

Electrolysis consists in passing an electric current through a solution, (brine in this case) of water and a salt to transform electrical energy into chemical transformation, that is to say by modifying the molecules.

The water molecule H_2O is broken, the hydrogen is lost in the form of gas, and the oxygen added to the salt to form a new molecule as in the example : $NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$

→ Calculator online (for hypocrites, chlorates and perchlorates) :
https://www.feanor-lab.com/calculator.php

2 - Solubility in water :

In g/100mL						
Temperature	**NaCl**	**KCl**	**$NaClO_3$**	**$KClO_3$**	**$NaClO_4$**	**$KClO_4$**
0°C	35.65	28	79.6	3.3	167	0.76
10°C	35.72	31.2	87.6	5.2	183	1.06
20°C	35.89	34.2	95.9	7.3	201	1.68
25°C	-	-	-	8.15	209.6	-
30°C	36.09	37.2	105	10.1	222	2.56
40°C	36.37	40.1	115	13.9	245	3.73
50°C	36.69	42.6	-	-	-	-
60°C	37.04	45.8	137	23.8	288	7.3

70°C	37.46	-	-	-	-	-
80°C	37.93	51.3	167	37.5	306	13.4
90°C	38.47	53.9	184	46	-	17.7
100°C	38.99	56.3	204	56.3	329	22.3
190°C				183		

3 - Electrodes :

The Anode (+) :

To withstand electrical potential, corrosion, and oxidation, you require a material that can meet all of these demands, and only a few options are available. The four primary materials commonly employed are :

- **Platinum**, very expensive and rare metal, 300 to 500mA/Cm^2 (near 700$USD/mL mid-2023)
- **Graphite**, cheap but which deteriorates quickly and defiles the brine, 30 to 40mA/Cm^2
- **PbO_2** is the most used in the past for perchlorates: it allows to pass from chloride (NaCl) to perchlorate ($NaClO_4$) in a single step until the end (the industry used about 4mm of thickness for a service life of 2 years → confirmed by experience.)
- **MMO** : (Mixed Metal Oxide) metal oxides, almost only on a substrate (Titanium), which are intermediate in price and keep a good life. 120 to 300mA/Cm^2
  IrO_2, RuO_2, PbO_2, MnO_2, Co_3O_4 ... (almost systematically with Iridium oxide).
  This is the category of MMOs has been used extensively in the industry and tend to be replaced by pure Platinum anodes.

NB: Platinum is suitable for perchlorates, but it degrades significantly faster when the remaining chlorate concentration in the brine is below 50g/L. Therefore, it is strongly advised to stop the electrolysis at this point to prevent the rapid degradation of the Pt anode.

NB n°2 : However, it is still possible to achieve this by reducing the lifespan of the platinum anode at a ratio of around 7 (≈15%).
I had some discussion with the highly skilled Canadian engineer : Richard Nakka who achieved a conversion of chlorate to perchlorate and stopped near 99.9% in a classical electrolysis cell with pure Pt anode. The rate degradation was near 33 grams of pure platinum per ton of $NaClO_4$ produced, which is significantly higher than the 4~6 grams commonly used in the industry.

The cathode (-) :

It is the one who releases hydrogen. This component simply must resist the brine corrosion. Commonly, the cathode is made of titanium (preferably « Grade 1 » for superior performance), or stainless steel types 304, 316 or 347.
Pure platinum also functions effectively, but it is unnecessary for this specific application.

Titanium : for some grades of titanium, (the presence of aluminum in the alloy ?) can tends to bend them on the opposite side to the hydrogen bubbles (creation of cavities in the alloy ?).
Avoid using cathode thicknesses less than 1mm unless the edges are well-supported.
Unfortunately, the titanium always bend a very little bit for the common thickness.

4 - Cell :

A cell is a device that has two electrodes (at least) : the Anode (+) and the Cathode (-) immersed inside an aqueous brine in a container.
NB : Total sealing is really difficult to achieve because of the very corrosive chlorine gases.

For chlorate / perchlorate application:

- The container is usually made of glass or borosilicate like pyrex (PE and PP plastics have a lifespan of only a few months. Polymers are not recommended except PTFE)
- A separation membrane between the electrodes is not necessary (although sometimes used when anode graphite is present, as it degrades rapidly and contaminates the solution), with the possible exception of the PbO_2 coating, which gradually disintegrates.
- It is usually necessary to provide a degassing tube for hydrogen gas (and Cl_2).
- The electrodes require a gas-proof connector to prevent the solution from rising by capillarity and causing rapid corrosion of the connections (within a few days). This is THE critical aspect of your cell. When I was just starting out, I tried various methods to achieve a good seal with glue, resin, sealant, plastic, and more. Unfortunately, none of these methods proved effective in the time (over a month).
Therefore, I developed a unique connector design that incorporates a shoulder and PTFE ring. This innovation has transformed the experience, eliminating any issues !
- If possible, the lid should be joined to the container, otherwise a salt crust forms slowly (nothing catastrophic, many don’t get seal because with months, Cl2 destroy almost everything, even silicons). The author's advice is not to waste time trying.
- The seals (ideally PTFE tape) must withstand the temperature of the solution AND Cl2 gas.
- An electrolysis cell poses a significant explosion risk in a confined space. It is advisable to place it outdoors in a secure area or within a controlled laboratory environment equipped with extraction pipes, fume hoods, or suitable technology.

5 - Lid :

This is the critical point of the cell !

The electrodes must be spaced 0.5 to 5 Cm from each other and fixed by a system that prevents the brine from soaking through by capillarity such as the use of my shouldering threaded connectors.

→ **My only recommendation is to use a PTFE lid and my shouldering threaded connectors.**
Of course it is more expensive but it is the way to get a durable cell.

However, if you are a beginner with a limited budget, I am providing you with the following outcomes from my initial tests. Enjoy ;-)

Experiments have shown that the material plated on the electrodes, such as removable silicone seals, epoxy resin, glue or many things did not work very well and therefore the liquid was able to infiltrate by micro-capillarity over the time.

Brine attacks a number of polymers and almost all metals especially on the Anode.
The clamps on the anodes oxidize quickly in a few tens of hours in contact with the brine.
You have to find the right glue or resin to seal the electrodes.

Conclusion after years of research : only PTFE (polytetrafluoroethylene) pressed against the titanium connector makes it possible to resist to liquid + gas infiltration because it is totally resistant and moreover, slightly flexible.

Warning : PE plastic and PP are not glueable by any common glue.
Most seem to stick but are very easily detached, especially after a while in this conditions.
Only very few proprietary glues succeed (many use powerful solvents like Xylene, quite toxic).

Here is the table of brine resistances of some materials :

Material	**Can work ?**	**Tested**	**Comments**
Vinylester Resin + MEKP	Yes	Yes	Seems to be the best one (resistance + corrosion)
Resin acrylic Two-compos.	Yes	Yes	Good adhesion + chemical resistance slowly degraded during weeks.
Glue T-7000 and E-6000	Yes+No	Yes	For a while, but slowly come off along the days
Acrylic glue with solvent	No	Yes	Not very efficient, some degradation and sticks badly titanium and allows infiltration
Resine Epoxy	Yes	Yes	Operates 1 to 2 months, surface is degraded rapidly and then less, used + of 4 months with few repairs
Polyester Resin	Yes+No	No	Probably works for a wile like weeks
Solvent polyurethane glue	Yes+No	Yes	Few experience, seems hold less than a week
Neoprene Glue	?	No	Probably poor resistance
PVC Glue	No	Yes	Dead in some hours
Acrylic putty (gun)	Yes	No	
DIY hot glue gun	No	No	
Plastic-fermit	Yes	No	According to a German client it is perfect
PE Plastic injection around connector	Yes	No	Used in industry for swimming-pool, but questionable for ClO3 + ClO4 ions

6 - Brine :

Theory :

In theory, any chloride can be transformed into chlorate and perchlorate.
In practice, difficulties are encountered for certain kind of chlorates/perchlorates : solubility, instability, adhesion on the cathode, rapid decomposition...

In pratice :

For most applications, it is common to start from table-salt: Sodium chloride (denoted NaCl); because of its solubility, its availability, its very low cost.
(Note : many of my client get trouble with bagged road salt, I can’t say if it is other chloride compound like CaCl or a particular ferrocyanide, but I strongly discourage you to use it).

Once the chlorate or Sodium perchlorate is obtained, it is generally transformed into another such potassium chlorate by metathesis (double decomposition) according to the equation:

$NaClO_3 + KCl \rightarrow KClO_3 + NaCl$

The weakly soluble $KClO_3$ (see table part 2) precipitates and the NaCl remains dissolved.

It becomes possible to filter the $KClO_3$ obtained.

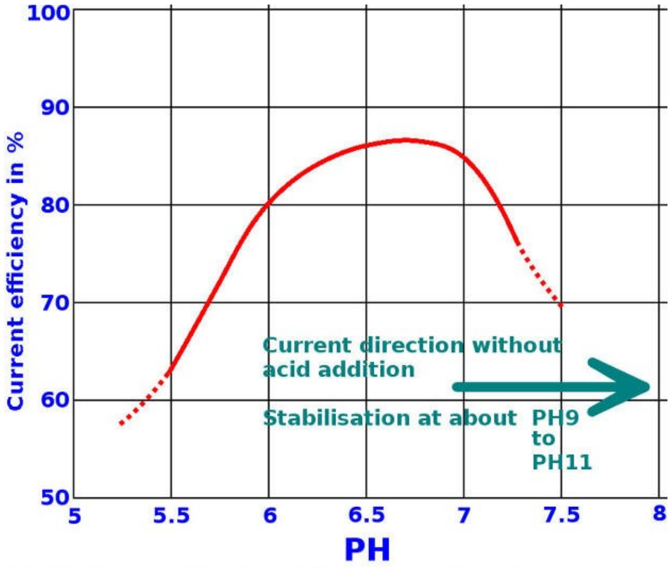
Additive :

Electrolysis tends to release chlorine, and thus, to form soda, NaOH (or X-OH), which remains in the brine and raises the PH.

This lowers the efficiency of the cell which goes down to 50% or 40%.

Furthermore, a high pH accelerates the degradation of the anode and even of the Ti cathode in the case of barium chlorate, for example.

To overcome this phenomenon, we must add an additive that allows a series of chemical reactions that will stabilize the pH and extend the life of the electrodes.



Conditions : 60°C, magnetite Anode, density : 30mA/Cm², NaCl : 230g/L, 2g/L Sodium Dichromate.

From Journal of Electrochemical Technology 6 (1968) 402

On this figure, you can understand easily the importance of keeping the pH near 6 to 7,5.

Below ~5 : the hypochlorite/chlorate can’t exist : acid destroy it and release chlorine.

There are different types of additives :

→ chromates: sodium/potassium dichromate, ... Used with stainless steel cathode.

→ fluorides: NaF, ... Used with stainless steel cathode (to be confirmed).

→ persulfates: sodium and potassium, suitable with titanium cathode, a bit less effective than chromates.

It is strongly recommended to use a persulfate salt which is a molecule much more accessible, often cheaper, and especially less toxic while being much more environmentally friendly.

For comparative performance of additive types, no reliable information has been found by the author to date. It seems that they are equivalent, globally, only their minimum quantity can vary.

It seem that stainless steel cathodes and the use of a chromate salt is slightly more economical than persulfate-titanium in terms of the quantity required.

Be careful, some types of anodes such as those containing oxides (PbO_2 / RuO_2 / IrO_2 ...) are incompatible with the presence of fluorine which degrades them.

Persulfate appears to be the most universal salt for laboratory anodes.

In general, concentrations of 2 to 4g/liter are used, I advise 4g/liter for some guarantee of pH stability.

7 - Electric power supply :

The control of current and voltage is a fundamental point of electrolysis.

Principle :

The electric current flows through the brine by moving electrons.
The quantity of passing electrons, the number of which is in coulombs, is directly related to the quantity of ions that will be modified.
Concretely: it is the ELECTRIC CURRENT per unit of time which will determine the final mass of product, and not the tension.

That is why the voltage is less important than current.
To get a simple stable voltage power supply is not enough at all. It can work, yes, but you won't control the current. In this situation most of the time your anode lifespan will be shorter.
Just sending 5VDC between electrodes can work, yes, but the current will probably be too high a part of the production and too low the other part.
You need a Power Supply Unit (PSU) that can limit the voltage (tension sent in open circuit : no load) AND limit the current, that is to said, it will automatically select the voltage below your maximum chosen value, to get your selected current.

With this kind of PSU, you know the amount of current flowing through the cell per unit of time (and like this, estimate the time of the end of your electrolysis run).
Luckily, we live in a wonderful time and it is possible to find very simple and inexpensive electronic modules that do this job. (During the twentieth century, it was much harder to control the current).
A simple constant-current module will keep you on a steady current and will adjust the voltage itself to achieve this task.
Before the start-up, in open circuit, you just need to set the maximum voltage allowed in output as protection.
For reference, it is near 5VDC in chlorate and 6VDC in perchlorate (the only goal is to protect your anode).

Circuit :

It is a direct current (DC) circuit that including many resistances in series :

1) resistance of the cables,
2) resistance of the connections to the electrodes (with corrosion, it can become extreme and even stop the current in some ours, because metal oxides are insulators)
3) resistance of the internal brine due to the gap-space (very low, don't worry about the distance)
4) resistance of the coating of the anode
5) threshold voltage drop of the formation of the molecule (near 2,6V, depend on some parameters)
6) resistance of the cathode surface (in some perchlorate cells, a white deposition occur on Ti-cathode)

Conclusion: if everything is well made, only the voltage drop of your chemical in formation will rise along time. For example when your NaCl pass slowly in $NaClO_3$ along days, at constant current, the voltage of your PSU will slowly rise by 0,8V for example.

Example :

The voltage for most electrodes should not exceed 3.5 to 4V. However, since the current passing through the wires of modest section develops a voltage drop, the maximum voltage of the power supply is generally limited to 5V for chlorate.
This value should be adapted according to your knowledge, electrode technology and your specifications or priorities.

A good electrolysis of chlorate with an MMO anode current density 150mA/Cm² is between 3.1 and 3.6V between electrodes (multimeter measurement).
If you are near 4.5V it become dangerous for your anode. Try to improve the parameters if possible (temperature, PH, current density, additive.).
The higher the voltage between the electrodes, the faster the natural degradation of the anode will occur.

Power supply :

My recommendations depend of your needs, scale, and budget. In any situation you need a “Constant Current” module.
→ *If you directly want the conclusion* of the whole paragraph : try to find a all-in-one PSU that take 110 to 250VAC in input and supply 0-6V or 0-12VDC and 0-40Amps with 2 potentiometers and 2 LCD (used on my videos and my big kits). It is all you need to working seriously at medium scale.

In 2023 (to be updated), for small inexpensive applications, the author advises some electronic modules called “DC-DC converter”, most of the time “Step Down” module.

1) Beginners :

A module based on a type XL4015 component that has a possibility of voltage and current adjustment. With possible LCD display current + voltage.

The maximum current indicated is 5A but depends on the temperature of the module.
For permanent use, without external cooling (heatsink, forced air or water exchanger), do not exceed 3 to 3,5A. (Under 4.2A the module lasts around 2 weeks at 12 ° C ambient).
A finger test shows if the operating temperature is acceptable: warm, maximum 40 to 50 ° C, or hot/burning, type 80/90°C in which case the electronics will probably not last more than one month.

2) Bit better :

A module like 12A 160W, a blue PCB with acrylic case named ZK-JVA-12KX used in my 10A MMO kit for perchlorate (at least until 2023) allow to clearly see the voltage and current, which is useful. Unfortunately, despite the 12A declared by the manufactured, it almost can’t go above 10A for an unknown reason. It is anyway a very good way to see everything, but need an active cooler above 7 to 8 amps.

3) <u>More powerful :</u>

For a little more advanced use, some 400W15A or 300W20A step down modules can be used to, including TO220 mosfets mounted on aluminum radiators. I used it for a wile but it is difficult to calibrate the current, and I had some problems with it. Now, after 2022, new modules appeared (still in 15~20A max near 5 to 15€) with better stability at low voltage as we need. You just need to supply it with a voltage above, like 12V for example, that can allow the required power (=Voltage x Amperes). I recommend the higher voltage possible in input like 40VDC to limit input current for same power.

4 <u>Laboratory classical PSU :</u>

For those who have a little more budget, (or want reliability) : a standard laboratory power supply, current regulated, with display, and cables, all in one, like those you used at school, is a convenient way. Current is often low, 5 or 10Amps. Above, price rise over 150€ easily.

Partial failure (personal experience on K3010D): look at the fan side probably to change, or switch 110 / 220V → desoldering the lead if you are 220V.

GOPHERT 5A without fan → perfect for several years (almost a decade now). Does not heat at room temperature, and pauses if the housing rises to 45/60°C, like in full sun.

<u>More current : modules in parallel ?</u>

ALL current regulators, theoretically, can be set in parallel.
This makes it possible to infinitely increase the current on a cell, even with small modules.
For complex reason, cheap modules of buck regulated constant current don’t works well in parallel. There are some bugs, things are weird, and fluctuations happen. It is an engineering operation, more complicated to do than we are thinking naively : it need common voltage reverence and shunt resistor in series.
This problem seems to disappear with high quality laboratory power supply in parallel.
I never get serious problems on short time of use. But the inversions of polarity and fusion of the poor connections has burned many of my modules !
In the end, this parallel method is not recommended, but it can help you temporarily if you have skills in electronic.

Cables :

The section of the cables is important. The power lost by joule effect is sometimes incredible and the voltage drop will be all the more obvious.

The cables sold with a cheap laboratory power supply are often of small section, type 0,3/0,5mm ² which gives, under 10A, losses often exceeding the 10W by heating uselessly. Furthermore, this heater can become a security problem.

It is therefore very important to over-size the sections, using heavy cable, even 2.5mm² rigid copper cable, which will be guaranteed up to 20A.
Shorten lengths to maximum and increase sections.

Example : I use 2x6mm² for 30amps to avoid useless looses and heating problems which lead to corrosion.

Clamps :

You shouldn't use clamp for a long time ! Only bolts are adapted !

The contact resistance of the clamps is sometimes quite giant, and is manifested by a palpable heating to the finger. For applications under 5A, small crocodile clips, very common, may be sufficient. Up to 10A, use larger tongs, preferably copper.
Beyond that, it is possible to multiply the clamps in parallel.

→ The best solution is to use my threaded connectors, otherwise, to bolt two copper plates, or zinc (or tin), on the electrode connectors.
A hole can be used to pass a bolt through the electrodes to tighten the plates/blades more easily, or simply pinch the electrode by the side.
Of course, the electrode wire or lead must be soldered or pinched onto these conductive and ductile metal plates.

If the connection oxidizes (naturally or by brine), it must be removed, sanded with sandpaper (emery cloth) and then put back on the electrode clean and washed.
If the connector become warm or burning, it must be removed and checked the contact surfaces.

8 - Temperature and acidity :

The temperature acts directly on the yield.

The higher the temperature, the better the performance of the cell will be good and reciprocal.

Unfortunately, the higher the temperature, the shorter the life of the MMO type electrodes. (Not for the Platinum a priori).

Several companies have given me values of 40°C to 100°C in use, for the same Ru-Ir coating but all have specified that the temperature reduced the service life, but without values.

Knowing that the industrial temperatures turn between 60 and 80°C in chlorate electrolysis for these coatings, and effective lifetimes of the order of 8000 to 20 000H; we can think that for small applications the consequences are hardly visible.

Another reason requiring a temperature above ambient temperature is that the first element that forms in the electrolysis is hypochlorite (active agent of the bleach).
A temperature > 40°C transform hypochlorite into chlorate according to the reaction: $3NaClO \rightarrow NaClO_3 + 2NaCl$.
Practically, the difference of a run starting below ~40°C and over is radical, the start almost no longer feels like chlorine, compared to a cold start.

→ Recommendation : keep the run temperature near 50 to 75°C, 60°C is very good, and don’t panic if too cold or over that.
I know some people which succeed to produce large batch cooled at 35°C with yields around 50% and other near 90°C without significant degradation of their anode after months.

Acidity affects the yield.

(Refer to the image part “N°6-Brine” about additive)
Without going into the chemical details, the chlorine that forms and releases itself from the cell produces equal part of remaining sodium hydroxide (NaOH, KOH, etc.) in the brine that will raise the pH, reduce the yield, and deteriorate the anode’s lifespan.
To overcome this slight emission of chlorine, we use the additive salts mentioned above (persulfate ...) and hydrochloric acid in industry.
Some amateurs add drops of HCl to the pipette from time to time but the operation remains difficult without any other equipment than PH paper 1-14.

→ Recommendation : after years of use and feedback from users, an initial amount in the brine of 4g/liter of persulfate (Na or K-Persulfate) with addition some times a day of some mL of fresh water at 2g/liter of persulfate to filling the evaporated water is perfect and "blocking" the pH close to 6.
Logically, the persulfate percentage depend of your evaporation level, but for 2Liter jar, 65°C and summer time (+25°C average), I add near ~100mL/day at 0,2% and near ~60mL/day at 0,4% in winter).
In this way, you don’t have to control the pH anymore.

→ Persulfate seems to be like “consumed” by the reaction over the time. I’m not sure that adding a larger quantity seems more beneficial than regular addition.
Refer to chapter N°9 subpart n°12 : the yield of my runs went from 59 to 70% by just adding more regularly the SAME quantity of persulfate (fresh water at 0,2% persulfate) : from 1 time/24H to 3 times (with about 10H for the night duration).
Permanent addition should be the better way…

→ Sodium bisulfate ($NaHSO_4$) seems to help too, I’m currently doing some tests. If you haven’t access to persulfate, I suppose that it is “better than nothing” but furthermore, as a very close molecule, it could probably improve the action of persulfate anyway.
The results are not amazing, it can just help. Further test will be done.

9 - Getting started for chlorate production (especially with MMO anode) :

By following every point below, I can guarantee perfect operation :

1) Use an electronic module, regulated (limited) in tension AND regulated in current that can suit to your anode’s surface. Send something like 100 to 200mA/Cm² of your anode for Ir-Ru coating.

Take your regulator module WITHOUT load wired on it, and adjust the maximum output voltage by selecting near 5V to protect your anode.
Then, cut off its input power, put a load in output (I advice something like 0,5ohm. Example 10 meters of power extension cord), or a wire in short circuit if your module allow it, then turn on the power, and select the maximum current to send in your cell.
If you don’t want or can’t calibrate your regulated current now, it is not a problem, you could do it later with the electrodes in the brine.
Then, cut off everything and connect your electrodes to your regulator.
→ Recommendation : be careful, a disconnection of the load on your regulator WHILE under tension (power on), can cause little sparks that can destroy your regulator’s component. I’ve burned some of them like this, thus, always connect and disconnect your load power off. (And repaired it by changing the PWM controller ship)

2) Put the connectors on the electrodes.
→ Recommendation, bolts with ring loop terminals on threaded bar, like my anode connectors.
(if your really want problems, you can use clamps as we all did at the beginning !)
Use a large section of copper cable to allow large current, example allow 6A/mm² maximum.

→ Anode (+): red wire of the power supply on the electrode covered with a dark/black and rough substrate for an MMO anode, (or other anode technology).
→ Cathode (-): black wire of the power supply on the titanium, nickel, stainless steel electrode...

3) Prepare your salt
In reality, it is almost impossible to reach the theoretical saturation for temperature.
So these empirical values can be used in mass by volume of brine:
→ NaCl: 270g/L, about 270g + 877mL of water (an easy way is 250g of NaCl/1000mL filled jar)
→ KCl: 350g/L, about 350g + 830mL of hot water (more water for ambient temperature).

4) Boil water in a container (or use the hot water tap), then pour in the salt and stir (for NaCl, use a clean-white table-salt source, not a road salt, which brings lot of strange reaction, chlorine releasing and pH problems).

5)Once the salt is dissolved, (small residues tends to not dissolve later...) add persulfate (Na or K) at a rate of 4 g/L of brine to be totally relax. (2 to 4g according to the sources, you can use less with experience).

6) When the brine is still warm, around 45/65°C, pour it into your cell jar.
(Warning to the thermal shock for the glass : borosilicate is strongly recommended)
Personally, I use everything in the same glass jar, I use this steps : NaCl + persulfate + 70°C hot water from hot tap + stirring and after 10/15minutes everything is dissolved and ready to start).

7) Put the lid containing the electrodes, spaced between 4 to 50mm on the top of your jar.
It is preferable to use a gasket between the lid and the jar, like PTFE tape, and evacuate gas through

a tube, but it isn't problematic at all to just lay the lid on the jar if you follow all this document's points : because "almost" no chlorine will be released, mainly the hydrogen gas.
Be strongly responsible about the environment, and keep this apparatus away from any source of flame/spark (risk of hydrogen explosion).

8) One time the lid is properly putted in the hot brine (near 45~65°C), you can now turn on the electric power.
Do not worry if the voltage reach the maximum selected at point N°5 above and if your current don't reach the maximum selected too. Usually, the cell's internal resistance is high at beginning and current will slowly rise in some minutes to reach your selected value, then, the voltage will decrease from the maximum to stabilize in something like 1 to 3 hours.
A correct parameter will give you 3,1 to 3,8V after stabilization.
(My MMO's kits of 100x50mm of surface gives 3,3V for 10Amps after 2hours in 900mL jar. Another example : my 200x60mm MMO, under 25 Amps, immediately start at 3,72V displayed on the PSU in 2Liter glass jar containing 500g of NaCl and 8g of persulfate and 45°C brine).

9) If the assembly is properly done, by putting your nose on the hydrogen outlet you will feel almost no smell of chlorine. Otherwise, you have room for improvement. (Despite permanent little chlorine smell is unavoidable)
→ If you precisely followed the above points, your solution will stay near pH 6~6,5.
If not, you have problems and your run is probably on the wrong way.

The stronger the chlorine smell and the higher the voltage, the less the cell is in good conditions.
In some cases, if too much chlorine is released in the first few hours, the brine will become very basic PH>9-10 and the voltage may rise to more than 4,5~5V between electrodes for MMOs. It is better then to cut it, (because you would damage the anode) and start it again by adjusting the pH with HCl or better : start everything with a new batch of salt (because the ionic "soup" is often impossible to repair for beginners, really. You better lose 0,1$/€ of table salt in new batch than 24Hours without results and damaging your anode).

10) After stabilization, like 2 hours for example, you can check and adjust the current flowing through the cell.
It is normal to get from 3.1V to 3,7V between electrodes (not the same as the regulator reading which include the voltage drop of your connection and your cable.)
You can allow a tension until 4,2V maybe, but for long anode's lifespan, I advise your to stay below 3,7V (still measured between electrodes). You can "play" with your current to adjust this tension.
During the run, along the days (usually), the voltage increases (for a constant current because your regulator maintains current by playing with voltage), to reach, near the end of your chlorate synthesis, something near 4,0V +/-0,3V between your electrodes, often something near 4,6V+/-0,3V read on the regulator.

11) Everyday (especially for beginners), check the level of the brine that evaporates, the temperature, the acidity (near pH6) the connection of the clamps/bolts (heating?) and the possible degradation of the Anode. With experience, everything will become stable and it just took 30sec of

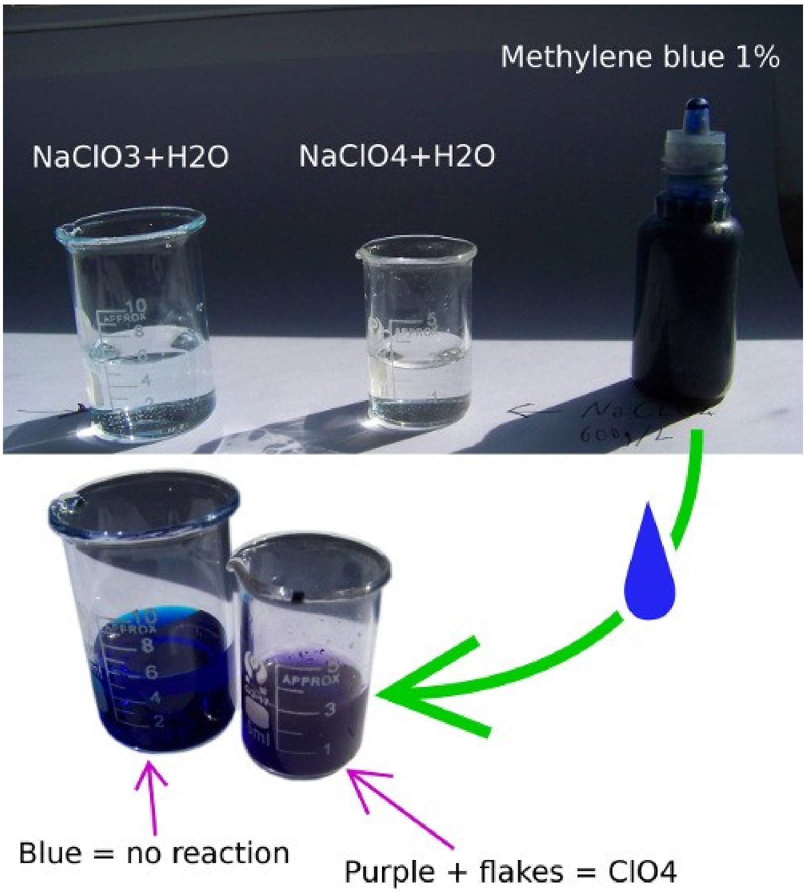
simple monitoring everyday.
(It is probable, with MMO anodes, especially at the first run, to get a very little brown deposition at the bottom of your jar. It could be impressive but it is a normal thing. If your pH is between 6 to 7,5 and your voltage below 3,9V between electrodes you haven't reasons to be worry.
With PbO_2 anodes, the degradation is very impressive, and I strongly discourage you to use this coating for chlorate production, as well as pure platinum : the degradation is very fast.)

12) Everyday (2 or 3 times per day if possible or more) add water to refill the evaporated liquid. Evaporation is a normal phenomenon. I strongly advise you to use 2g/liter (0.2% solution) of persulfate in this "daily filling water" to help to stabilize your brine at pH near 6. (For larger jar, like 5liters, I advice you to use 4g/liter of persulfate in this "daily filling water".)
If your goal is to reach the chlorate saturation at the end of your run, it is the opportunity for you to add NaCl solution at this moment. Without experience, you shouldn't jump on this advanced operation that need calculations and control.
→ Yield : I made several runs of same jar : 2Liters, 500g of NaCl and 8g/Persulfate, 25Amps, and by refilling evaporated brine 1 time/24H, I get 59% of yield (apparition of purple in methylene blue test) and get near 70% of yield by refilling 2 to 3 times/24H. Thus : the frequent addition of persulfate really improve the yield. A permanent addition is the better route.

13) If you use some salts like KCl, avoid that the crystals of chlorate poorly soluble as $KClO_3$ reach the anode, they could scratch or hang on it and deteriorate the coating (if MMO …).
I recommend to not produce $KClO_3$ directly from KCl salt because the tension on the anode is greater, thus, the lifespan of your anode is a bit shorter, it is complicated to get pure chlorate, there is often the basic KOH remaining in the crystals, and the anode is often locked in crystals (it is hard to remove).
I suggest to stay on NaCl electrolysis, and at the end : use the double displacement (metathesis) as explain under in this document.

14) End of your run
→ My online calculator : https://www.feanor-lab.com/calculator.php
Besides the theoretical time calculation, you have many signs which indicate the end of the electrolysis :
- The voltage of the regulator is something around +0,5V than the beginning.
- The anode (and cathode) bubbles are really more numerous and bigger.
- The solution if more transparent.
- Drop a drop of 1% methylene blue into the brine (or into a few milliliters of brine).

If the brine remains blue: no perchlorate
If the brine turns purple and forms flakes: presence of perchlorate.



You can then pour back the flask test in the brine, the dye will disappear soon.

10 - Calculations :

I coded this page for you : http://www.feanor-lab.com/calculator.php

Electrolysis of chlorate:

6 coulombs/mol (2 coulombs/mol oxygen) = 96 485*6mol/3600Sec = 160.8A/H/mol
$NaCl \rightarrow NaClO_3$ = 2.752A/H/g NaCl in brine = 1.511A/H/g final gram of chlorate
$KCl \rightarrow KClO_3$ = 2.157A/H/g of KCl in brine = 1.312A/H/g final gram of chlorate

In other words : if the NaCl brine is passed through by 2.75 amperes for 1 hour, 1g of NaCl will be changed to 1.821 g of sodium chlorate in the molar ratio between NaCl and $NaClO_3$.

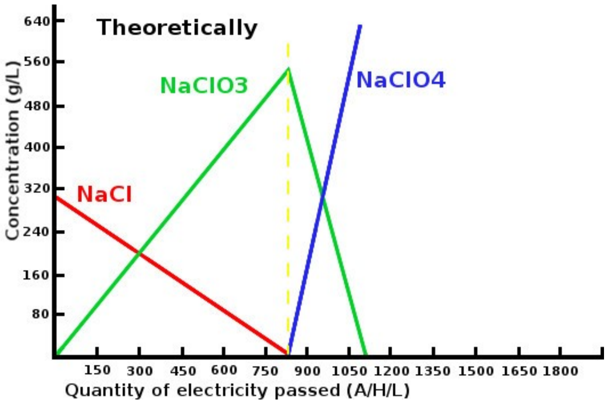
Perchlorate electrolysis: (in one step) :

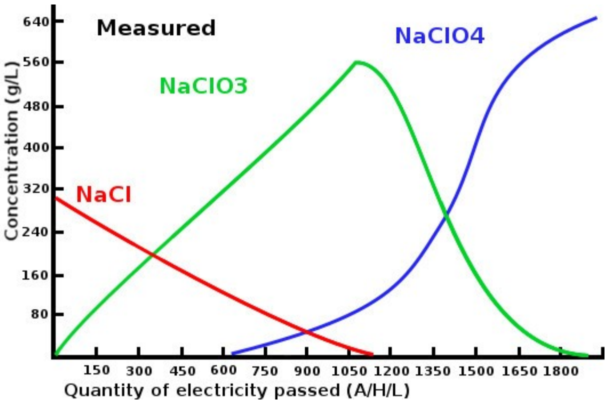
8 coulombs/mol (2 coulombs/mol oxygen) = 96 485*8mol/3600Sec = 214.4A/H/mol
$NaCl \rightarrow NaClO_4$ = 3.669A/H/g of NaCl in brine = 1.751A/H/g final gram of perchlorate
$KCl \rightarrow KClO_4$ = 2.876A/H/g KCl in brine = 1.548A/H/g final gram of perchlorate

(Perchlorate need higher current density. It is more difficult to obtain than chlorate for different technical reasons.)

For a realistic calculation, it is necessary to use the practical efficiency of the cell.
An amateur cell without stabilization additive, without control of the PH and low temperature turns in the 30-50%.
A good amateur chlorate cell goes up to 75%.

Two theoretical and practical comparative tables :





We can seen that the formation of perchlorate is not simultaneous with the disappearance of NaCl. With years of experience, I can say that my right graph is a bit exaggerated : the moment apparition of violet under the drop of methylene blue correspond to the end of chloride very closed to 0%, I'll confirm that point with measure test in a future.

The slight rise of the voltage at the end of chlorate is a very evident indicator of perchlorate formation : in my usual setup, the voltage is passing (on PSU display, and for a constant current of 25A) from 3,72V at beginning, to gradually 4,15V at the end after 80 hours, and suddenly, in some hours, at 4,25V.

But this indicator is only valid in a stable environment. It can be unfortunately also caused by other factors : oxidation of the cathode, changing PH, temperature, oxidized connections ...

<u>NaCl example :</u>

Per hour				
Current	**Yield 50 %**		**Yield 80 %**	
	NaCl consumption	$NaClO_3$ produced	NaCl consumption	$NaClO_3$ produced
2A	0,363g	0,662g	0,581g	1,059g
3A	0,545g	0,993g	0,872g	1,588g
4A	0,727g	1,324g	1,163g	2,118g
5A	0,908g	1,655g	1,453g	2,647g
8A	1,453g	2,647g	2,326g	4,236g

10A	1,817g	3,309g	2,907g	5,295g
15A	2,725g	4,964g	4,360g	7,942g
20A	3,634g	6,618g	5,814g	10,589g
25A	4,542g	8,273g	7,267g	13,237g

Note: the yield drops seriously at the end of electrolysis, so there is always a little amount of NaCl remains in the end, if you stop at chlorate.
It is therefore necessary to continue the electrolysis beyond this time if you wants to reach a final low rate of remaining NaCl.

11 - Double-displacement/metathesis :

It is very common to obtain another chlorate/perchlorate salt by a very interesting chemical property: metathesis otherwise called "double decomposition".

This operation exploits the difference in solubility of each product.
It consists of starting from a soluble salt such as NaClO3 and adding a saturated solution of another salt (or simply pure salt powder) such as KCl in order to obtain the precipitation of the new chlorate or perchlorate .
Example : $NaClO_3 + KCl \rightarrow KClO_3 + NaCl$

Several reasons justify this operation in favor of NaCl salt (by opposition to KCl used by some users from the start of the electrolysis) :
- The solubility of NaCl, and even more of its chlorate and perchlorate
- The longer lifespan of the anode in NaCl than other chloride like KCl
- The possibility of filtering the brine when it is soiled by deposits of the anode (graphite, PbO_2...) and obtain pure crystals after metathesis.
- The health aspect and non-danger of NaCl, compared to other salts (BaCl, NH_4Cl ...)
- The technical control of this type of electrolysis easier than other salts (BaCl, SrCl ...)
- The low cost of NaCl
- The infinite recycling facility of the initial brine
- Mandatory for certain insoluble perchlorate ($KClO_4$), due to the impossibility of obtaining directly.

For this operation, it is necessary to put the same number of moles of desired salt as the amount of initial NaCl salt.
For 1 mol of NaCl: 58.44g electrolyzed to chlorate, 1 mol of KCl: 74.55 g should be added.
A small excess may be advantageous, like 1,1mol to be added per 1 mol of initial salt, the surplus will remain dissolved in the final liquid.

To recover a maximum of crystals : cool down the solution as low as possible, such as 0°C or below.
A freezer may be useful since the dissolved salts will lower the freezing point well below 0 ° C, and the chlorate + perchlorate crystals will become increasingly insoluble for the most part.

To produce $KClO_3$; I suggest you to use the way of NaCl electrolysis, stop the run before the apparition of purple in your methylene blue test, and add equivalent molecular KCl from your initial NaCl and then, cool your product near 0°C or below if it is possible, then, centrifuge your crystals with a high-performance machine, at least at 1000G during long minutes. In this way, only a very tiny trace of water + NaCl will remains, the chloride will be below 1%.
But if it still too much, you can wash your $KClO_3$ crystals again with 0°C water and centrifuge your product again. Your liquid could be recycling and your $KClO_3$ could reach 99,9% in this way, by loosing a bit of mass by dissolution in the water.

Example For 100g of initial NaCl to pass into $KClO_3$ or $KClO_4$:

1 - Prepare 127.6g of KCl in powder for each 100g of initial NaCl (NaCl/58,44*74,55)
2 - Add this mass of KCl in the electrolyzed brine (the total minimum brine's volume should be near 350mL to 400mL/100g of KCl added, the temperature influence the solubility's ratio)
3 - Stir until a very fine homogeneous powder is obtained in the jar.
4 - Put in a very cold place (fridge, freezer …) After a while, crystals will continue to form.
5 - Filter the white crystals in suitable filter: cloth, coffee filter, laboratory filter...
6 - If possible centrifuge the product to remove water, otherwise, you can absorb it with clothing.
7 - The purity without centrifuge is near 98% contaminated with NaCl
8 - For higher purity, you can wash it with water and centrifuge again to rise over 99,5% for $KClO_3$ and more than 99,8% for $KClO_4$.
9 - Dry it in hot place, oven is suitable for $KClO_4$ but not for $KClO_3$ because it will corrode the metallic parts ;-)

12 - Chemical properties :

Properties of chlorates :

Chemical formula : $NaClO_3$/$KClO_3$
Molar mass : 106,44(Na) and 122,55g(K)
salts : NaCl : 58,44g and KCl : 74,55g
Density : 2,54@20°C (Na) and 2,32(K)
Fusion : 248–261°C(Na) and 356°C (K)
Evaporation : 300-400°C(Na) (decomposition) and 400°C (K) (Decomposition)
Solubility : Na : glycerol, hydrazine, methanol, and slightly ethanol acetone and ammonia.
K : Glycerol, almost insoluble acetone and ammonia.
Reactivity: be careful, powerful oxidizers, used in pyrotechnics, but relatively sensitive to acids and shocks. "Never" use sulfur because the formation of sulfuric acid in the presence of moisture can lead to spontaneous explosions (cause of several fatal accidents).

Properties of perchlorates :

Chemical formula : $NaClO_4$ and $KClO_4$
Molar mass : 122,44(Na) and 138,55g(K)
salts : NaCl : 58,44g and KCl : 74,55g
Density : 2,50@20°C (Na) and 2,52(K)
Fusion : 468°C(Na) and 610°C (K) (decomposition starting near 400°C)
Evaporation : 482°C(Na) (decomposition) decomposition (K)
Solubility : Na : water, methanol, ethanol, acetone, ethyl acetate.
K : water (100 times less than $NaClO_4$) and virtually no other solvent ?
Reactivity: strong oxidants, more stable than chlorate in temperature + chemically. May be mixed with sulfur. Represent a greater security in the pyrotechnic fields.

<u>13 – Sodium perchlorate electrolysis</u>

Principle :
-> As mentioned above :
$NaCl \rightarrow NaClO_4$ = 3,669A/H/g from NaCl in brine corresponds to 1,751A/H/grams of final $NaClO_4$

Warning: the electrochemical synthesis of perchlorate is <u>more difficult</u> than that of chlorate!

<u>a) There are 2 methods :</u>

→ The anode's technology determine the method
1 – By starting from sodium chlorate $NaClO_3$ already dissolved in solution at 700/750g/Liter previously obtained by an MMO anode, and run again this brine with another electrode technology (strongly recommended).
2 – Starting directly from NaCl table-salt to end in $NaClO_4$ (more uncertain in reality).
(→ note that from now, I no longer waste time helping people who have problems with this method)

1-a) The simplest and cheapest route is to use a pure Titanium anode coated with PbO2: lead dioxide.
1-b) With years of experience, many of us opted for the use of a platinum anode, pure for well plated with a thick thickness.

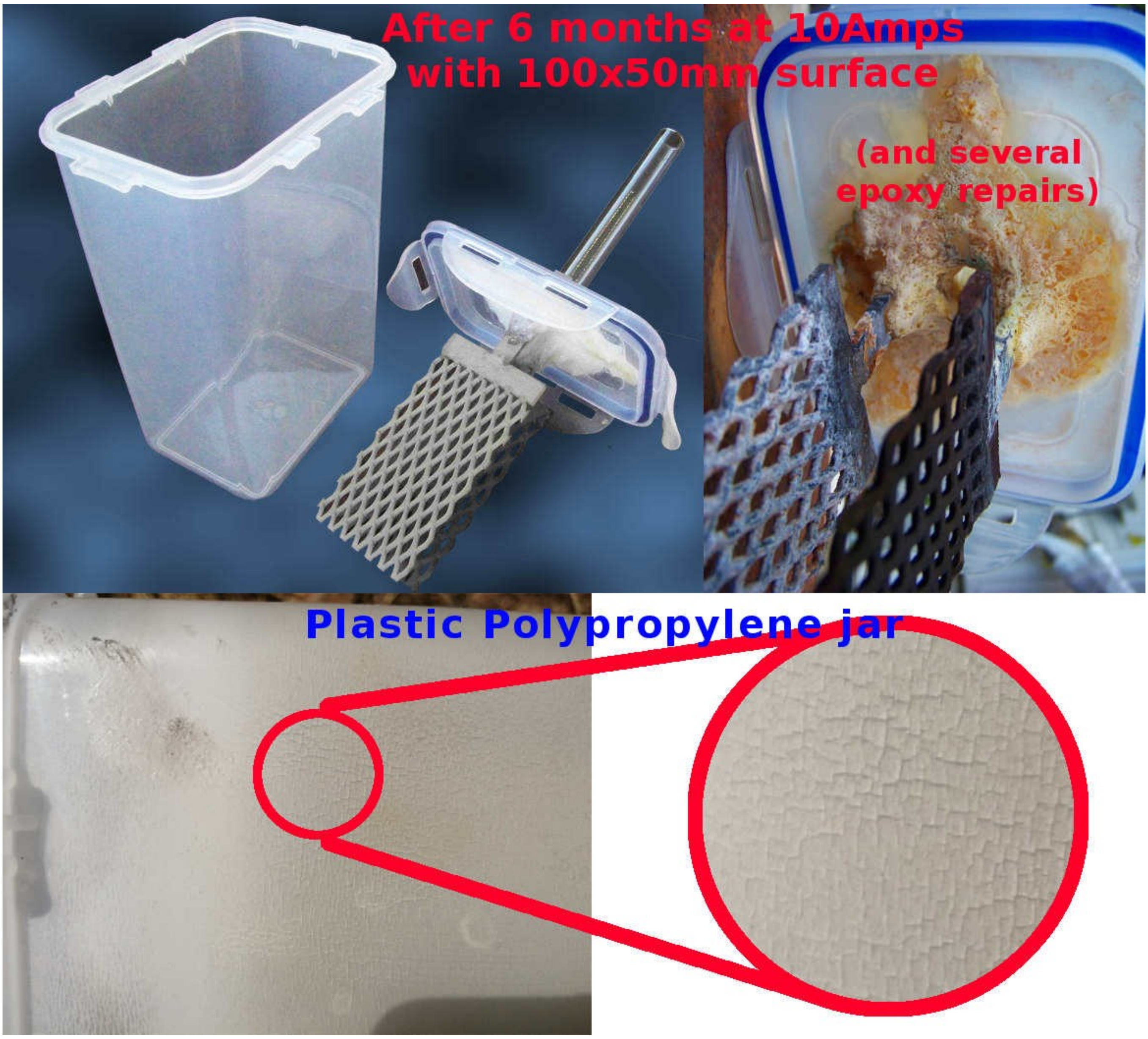
PbO2: it allows electrolysis to run up to almost 99,9% $NaClO_4$ in one step, unlike Platinum which degrades significantly below 50g/L of remaining $NaClO_3$, BUT both allow 99,9% anyway, it's all a question of compromise.
Additionally, PbO2 coating is cheap unlike Platinum. However, it is slightly toxic for the

environment, and must be recycled or thrown away with lead vehicle batteries (used in thermal engines: cars, motorcycles, boats, planes, etc.)

b) Behaviour :

The PbO2 anode generally has a coating of 0.1 to 4mm.
This coating slowly degrades to diffuse into the brine and produce brown contamination.
The dark color appears quickly, as well as a brown deposit at the bottom, you should not worry.

For the photo taken below, the set operated for 5 to 6 months at 200mA/Cm^2 for an initial thickness of around 0.25mm, and there is still enough to operate for some months.
(the epoxy resin had to be added several times to counteract degradation and infiltration).



Here, old problematic PbO$_2$'s lid version :
1) Electrodes were built with plate connectors (brine's infiltration on long-term)

2) The polypropylene jar was not suitable at all for long time, and the resin, (degradation of the plastic)

c) Now, the better and simplest way :

1) I added a new design with threaded connectors : the shouldering allow a pressure on PTFE washer or plate, and thus, avoid the brine + chlorine gas infiltration.
(now in 2024, since one year, some companies copy and sell my anode's model with the exact pictures of my electrodes including the quotation draws… It is not fair-play, I should contact them...)
2) Glass jar is the better option for long term use.

d) Yield :

Le $NaClO_4$ a un moins bon rendement lors de la synthèse que les principaux chlorates. Cependant, avec une anode en PbO2 il est possible d'atteindre les 50 à 60 % sans trop de difficultés, pour une concentration finale > 90 % du perchlorate possible (3A/Heure/Gramme de perchlorate de sodium final à environs 58 % de rendement de Courant, soit dans les 18KW/H/Kg sous 6V…)

Quatre facteurs sont importants :
1 – La température (60-65°C recommandé, mais déjà utilisé à 75-80°C plusieurs semaines sans grosse dégradation visible)
2 – L'acidité (garder le PH autour de 6,5 comme pour les chlorates)
3 – L'additif (persulfate, Fluorure ou chromate) pour améliorer le rendement voir même « permettre » la formation de perchlorate (voir liste des problèmes plus bas).
4 – La concentration de ClO_3 : en effet, la concentration doit être élevée, pour un bon rendement 700 à 750g/L de $NaClO_3$ minimum.

Il est donc conseillé de compléter l'eau de l'évaporation par de la saumure à saturation, en quantité connue, afin de monter la concentration finale à environs 500g/NaCl/Litre d'eau par exemple.
(Il est possible avec quelques difficultés, d'atteindre environs 600g de NaCl/L initial pour une solution finale proche de 2Kg de $NaClO_4$/L d'eau restant.)

Un autre facteur qui agit sur le rendement est la densité de courant par unité de surface, il semble qu'un courant important est favorable au rendement, mais pour toute anode, à partir d'un seuil, la durée de vie diminue.
Peut-être est-ce la raison pour laquelle le Platine a un rendement (en courant) un peu meilleur que le PbO_2 puisque ce métal noble permet de monter à 500mA/Cm².

e) Protocol for the one-step method :

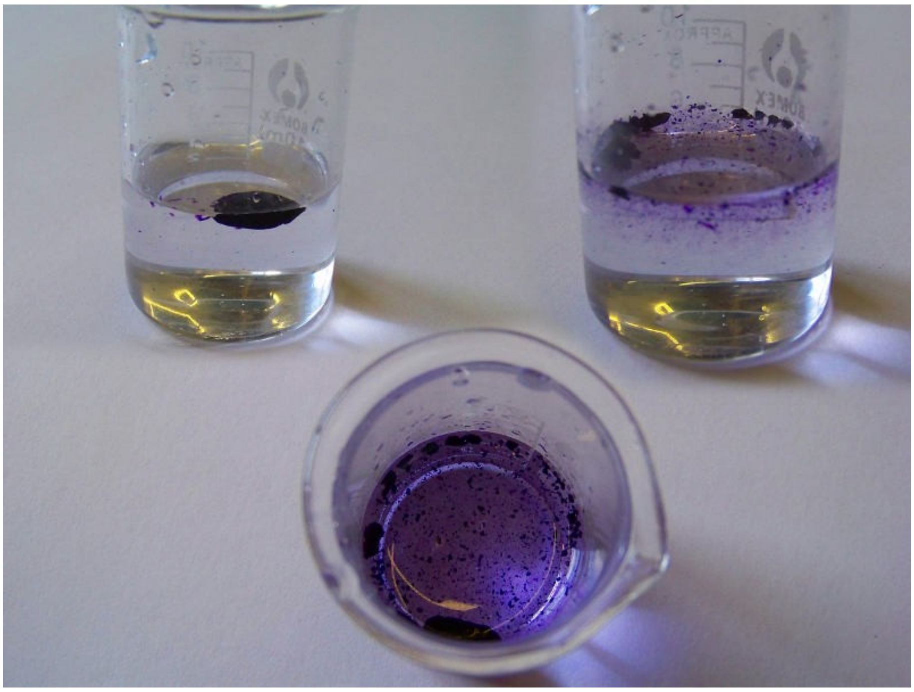
1 – Préparer le volume maximal d'eau (distillée de préférence) à mettre à chauffer à ébullition.
2 – Verser environs 270g de NaCl par Litre d'eau chaude.
3 – Laisser refroidir un peu pour atteindre 50 à 60°C, puis ajouter 2 à 4g/L de persulfate de potassium ou sodium (ou un autre composé plus toxique mais probablement plus efficace comme le NaF)
4 – Lancer l'électrolyse à 200 à 300mA/Cm² (200mA recommandé) dans un récipient de verre ou pyrex de préférence (borosilicate), car la durée de vie de presque tous les plastique est limitée.
5 – Vérifier la tension et maintenir le courant constant. La tension est entre 3,5 et 4,5V au démarrage en général.
6 – (*Facultatif : préparer une autre solution à 270g/L de sel NaCl à dissoudre dans le même volume d'eau froide (sans importance ici) et l'acidifier à l'HCl. Si vous ne connaissez pas votre cellule, utiliser environs 1mL d'HCl pur équivalent pour 100mL qui dépend surtout de la vitesse d'évaporation. Enfin, ajoutez 2 à 4g/L de persulfate dans cette saumure, qui vous évitera que l'électrolyse reste « bloqué » au stade chlorate indéfiniement.*).
7 – Compléter l'évaporation graduelle par la saumure précédente (facultatif) ou de l'eau acidulée à environs 1 % de HCl pur (à adapter empiriquement), au fur et à mesure des jours.
8– Déterminer la fin :

– La tension entre électrode (toujours différente de celle de alimentation à cause la chute de tension dans les câbles) monte au passage du perchlorate et atteint 4,5 à 5,5V lorsque l'opération est terminée, normalement (cela dépend des formes d'électrodes et de leur distance). Ne pas dépasser les 5,5V la dégradation du PbO_2 deviendrait très rapide.

– Lorsque le récipient passe de marron à totalement transparent, que la poudre de PbO_2 en suspension retombe au fond du récipient en moins de 1H sans remuer c'est le signe que votre concentration en $NaClO_4$ est très bonne (proche du maximum).

– Test : faire tomber une goutte de bleu de méthylène à 1 % dans quelques mL de saumure. Cette fois, si vous avez du perchlorate presque pur, vous n'avez « presque aucune » coloration en violet de la saumure mais « uniquement » des paillettes violettes. C'est le signe qu'il n'y a presque plus de chlorate.

– Lorsque l’ajout d’une solution d’HCl à 1 % (ou plus), ne dégage pratiquement plus de bulles de chlore, la concentration de chlorate est très base.
9 – Le NaClO4 en solution concentrée (100 à 200g/100mL) est visqueux, ne mouille pas, est presque huileux, et se sépare tout seul de la poudre de PbO2. Il n’y a donc pratiquement plus besoin de filtrer la saumure, il suffit de la verser et de garder la partie basse, très concentrée en suspension de PbO2 puis filtrer ce reste aisément.



→ Le NaClO4 est très hygroscopique et n’existe sous sa forme anhydre (totalement sèche) que s’il a été chauffé au dessus de 130°C environs.

f) « Blocking-problem » in “one-step method” NaCl → NaClO4 :

Expérience de l’auteur : après de nombreux cycles dans des conditions très proches, certains se sont déroulés parfaitement avec des très bonne concentrations pour 58 % de rendement et d’autre… Impossible d’obtenir du perchlorate.

Problème fréquent → L’électrolyse reste bloquée en chlorate.

Solution → Une présence de 2 à 4g/Litre de persulfate dans la saumure de maintient de l’évaporation permet d’éviter ce problème la plupart du temps si les conditions sont stable.

Description du problème : si, arrivé à 60 % du temps théorique pour passer du NaCl en NaClO3 le test de bleu de méthylène reste négatif : totalement bleu, aucun violet. Alors c’est mauvais signe.
→ Il vous faut remettre le PH à 6 ou 7 avec de l’HCl, et surtout ajouter une nouvelle fois du persulfate : 2 à 4g/litre et bien remuer.
→ Sortir les électrodes et frotter la cathode au besoin pour la décalaminer.

Si le test de bleu de méthylène ne survient toujours pas rapidement, en dessous de 50 % théorique, stoppez la solution, filtrez le dépôt de PbO2, reprenez le protocole ci-dessus en ajoutant une nouvelle fois du persulfate.

Si au bout de 3 tentatives et en dessous de 40 % du rendement théorique électrique (en courant) vous n’avez toujours pas de violet, alors le problème est ailleurs : votre indication de courant est peut-être fausse, vos calculs sont erronés, … Vous devriez recommencer à zéro et suivre précisément le protocole, renseignez-vous sur internet.

g) Chlorate destruction :

Utilité : pour la plupart des applications, il est important que le perchlorate soit exempt de chlorate résiduel qui, dans certains cas, peut s’avérer très dangereux (compositions de feux d’artifices au soufre, perchlorate d’ammonium…).

Il est souvent nécessaire de détruire les molécules de chlorate par différents moyens :

HCl (acide chlorhydrique) :

L’attaque du produit brute par un acide fort détruit le chlorate en dégageant du chlore, toxique et dans certains cas explosif.

Méthodes « brute » :
N°1 : Mélanger de l’HCl concentré type 30 % avec un volume identique de saumure concentrée et laisser l’acide régir avec le chlorate pendant plusieurs heures. Certains mènent la solution à ébullition pour accélérer la réaction.

N°2 : Verser environs 25 % de la masse du NaClO4 brute sec d’HCl (20 à 35 %) et laisser agir plusieurs heures jusqu’à la fin de la réaction.

N°3 : Pour une solution à forte concentration de NaClO4 et peu de NaClO3 résiduel, n’ajouter de 5 à 10 % d’HCl (concentration 20 à 30%) et laisser le chlore s’évaporer pendant quelques temps, plusieurs jours en général, dans un endroit ventilé et adapté.

→ Faire évaporer l’HCl par chauffage ou sous vide partiel, avec du matériel de laboratoire adapté.
→ Laisser l’acide pour la méthode du KClO4 par double décomposition, puis laver les cristaux obtenus par la suite avec de l’eau (un minimum pour ne pas trop dissoudre de produit).

Pour retirer l’acide : voir le paragraphe ci-dessous « neutralisation »

Métabisulfite de sodium :

(méthode identique, à priori, pour le Sodium Bisulphite/Sodium Sulphite/Sodium Disulfite)
- Ajouter des gouttes d’HCl dans la saumure pour atteindre un PH de 3 ou moindre.
- Ajouter une masse de métabisulfite proportionnelle à la quantité de chlorate. Commencer progressivement, par 5g/Litre dans le cas d’une bonne électrolyse aboutie.
- Chauffer l’ensemble pour accélérer le processus.
- Vérifier la présence de chlorate.

→ Au carmin d’ingido : une goutte de carmin à 1 % en solution dans quelques mL de solution : si la couleur reste bleu, les traces de chlorate sont infinitésimales, si la couleur disparaît en quelques secondes, il faut ajouter du méta/bisulfite.

h) Neutralisation (désacidification) :

Pour les solutions :

Ajouter progressivement du bicarbonate (de sodium ou potassium) en poudre fine, ou bien à de l'hydroxyde de sodium ou potassium.
Vérifier le PH et laisser la solution légèrement basique, >7,5, par sécurité.

Pour le KClO4 en poudre :

Terminer le lavage avec de l'eau froide à 5 % de bicarbonate pour détruire toute trace d'acidité.
Cette solution doit être en faible quantité, et proche de 0°C pour ne pas trop dissoudre les cristaux.
Une fois le KClO4 sec, ajouter 0,5 % de bicarbonate de sodium ou potassium, en poudre fine, dans le produit finit pour la conservation, par sécurité.

→ Take in note that all perchlorate are endocrine disruptors and a serious problem for the environment regarding this point because it can't be degradated easily and naturally like chlorate for example.
Thus, please, recycle your brine or discard it in a special chemical center. If you can't : evaporate everything and burn it in security, the planet will thank you !

14 – Potassium perchlorate $KClO_4$

Potassium perchlorate can't be made directly via electrolysis because of its very low solubility (17g/Liter of water at 20°C).
You have to produce sodium perchlorate first, then, use double metathesis : equimolar ratio of your initial NaCl salt used, as seen in the chapter 11.

1,276g of KCl is needed for each grams of NaCl before the electrolysis.
Or 74,55g of KCl for 122,44g of pure NaClO4 dryed in oven at 150°C during 1 or 2 hours with enough water to dissolve your remaining NaCl + security, example :

1) 1Kg of pure NaClO4 (or 1147,1g mono hydrate dried at 100°C)
2) 1770mL of water is added and stired.
3) 608,9g of dry KCl is added.
4) Everything is mixed and be rested some hours.
5) The mixture including a white powder is filtered in a large filter like synthetic fabric.
6) The collected powder is preferably centrifuged, otherwise some tissue can absorb water as much as possible.
6,5) A second wash can be used to remove the NaCl contamination, for example 1Kg of water for 1Kg of theoretical final powder could lead you over 99,5%.
7) The final past is dried, this time, electric oven is possible if you are sure that no chlorate trace are present anymore.

→ Take in note (same than $NaClO_4$) that all perchlorate are endocrine disruptors and a serious problem for the environment regarding this point because it can't be degradated easily and naturally like chlorate for example.
Thus, please, recycle your brine or discard it in a special chemical center. If you can't : evaporate everything and burn it in security, the planet will thank you !

15 - Ammonium Perchlorate NH_4ClO_4 :

There are 2 main ways to produce ammonium perchlorate :
1) The Ammonium chloride NH_4Cl (Youtube video here) page : 27
2) The Ammonium Nitrate NH_4NO_3 page : 27

The common industrial method uses NH_4Cl, but better yield has been achieved with the nitrate salt, due to greater solubility of the final by-product (solub. $NaNO_3 >> NaCl$).

Synthesis of ammonium perchlorate with ammonium chloride :

From pure ammonium nitrate and pure sodium perchlorate (anhydrous).

$NH_4Cl + NaClO_4 \rightarrow NH_4ClO_4 + NaCl$

Final solubility : at 0°C only 0.164mol/167mL of NH_4ClO_4 can be dissolved against 1.43mol/167mL for $NaNO_3$ at 0°C. It is therefore possible to lower the volume of water a little more.

For 1mol (example):
→ 1 mol of $NaClO_4$ = 122,44g (heated over 140/150°C to become anhydrous)
→ 1 mol of NH_4Cl = 53,49g
→ 200mL of water

1) – Dissolve the two anhydrous powders in water (distilled), and stirr. A white powder rushes.
2) – Cool the jar to -10°C to optimize the crystallization yield. (Colder possible = better yield, so -10°C if you can is the must, or the point just before solidification of the brine).
3) – Filter it.
4) – Centrifuge the crystals (to remove the contaminant brine).
5) – Optional : another step of washing of the crystals with distilled water and another centrifugation, to allow greater purity at the cost of mass loss.

NB : the perchlorate ions are an endocrine disruptor, they are pollutant, the nature is not able to break the stable ClO_4 ions contrary to the ClO_3 : please, don't throw your brine.
Respect the environment.
If you haven't recycling solutions : dry and burn it, it is the better way.

Result : empirically 70% of NH_4ClO_4 crystals are obtained by this way at 0°C (give a room for improvement).

Synthesis of ammonium perchlorate with ammonium nitrate :

From pure ammonium nitrate and pure sodium perchlorate (anhydrous).

$NH_4NO_3 + NaClO_4 \rightarrow NH_4ClO_4 + NaNO_3$

Final solubility : at 0°C only 0.164mol/167mL of NH_4ClO_4 can be dissolved against 1.43mol/167mL for $NaNO_3$ at 0°C. It is therefore possible to lower the volume of water a little more.

For 1mol (example):
→ 1 mol of $NaClO_4$ = 122,44g (heated over 140/150°C to become anhydrous)

→ 1 mol of NH_4NO_3 = 80,04g
→ 167mL of water

1) - Dissolve the two anhydrous powders in water (distilled), and stirr. A white powder rushes.
2) - Cool the jar to -10°C to optimize the crystallization yield. (Colder possible = better yield, so -10°C if you can is the must, or the point just before solidification of the brine).
4) – Centrifuge the crystals (to remove the contaminant brine).
5) – Optional : another step of washing of the crystals with distilled water and another centrifugation, to allow greater purity at the cost of mass loss.

NB : the perchlorate ions are an endocrine disruptor, they are pollutant, the nature is not able to break the stable ClO_4 ions contrary to the ClO_3 : please, don't throw your brine.
Respect the environment.
If you haven't recycling solutions : dry and burn it, it is the better way.

Result : 83.6% of NH_4ClO_4 crystals are obtained by this way at 0°C (from 77 to 84% depending on the temperature).

References :

My own website : www.feanor-lab.com

Chlorate synthesis via electrolysis (2021) : https://youtu.be/0aBQqFC_hzU?si=ZbeLQbVbf1KK7Wh7

Ammonium perchlorate synthesis, video tutorial (2021) : www.youtube.com/watch?v=QvFt8myD7Gs

Potassium perchlorate synthesis, video tutorial (2021) : www.youtube.com/watch?v=cxmuHoh7ObM

Barium chlorate synthesis, video tutorial (2021) : www.youtube.com/watch?v=UQ4nW_4MsJc

Very skilled chemist : http://www.chlorates.exrockets.com/chlorate.html