

Practical guide to chlorate/perchlorate electrolysis

Laboratory guide of informative and technical nature.

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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 H₂O 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 : $\text{Na}^+ \text{Cl}^- + 3\text{H}_2\text{O} \rightarrow \text{NaClO}_3 + 3\text{H}_2$

2 - Solubility in water :

Temperature	In g/100mL					
	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 resist the electrical potential, corrosion and oxidation, you need a material that supports all these constraints and there are few. The four main ones used are :

- **Platinum**, very expensive and rare metal, 300 to 500mA/Cm²
- **Graphite**, cheap but which deteriorates quickly and defiles the brine, 30 to 40mA/Cm²
- **PbO₂** is the most used in the past for perchlorates: it allows to pass from chloride (NaCl) to perchlorate (NaClO₄) 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, monobloc or on a substrate (Titanium), which are intermediate in price and keep a good life. 200 to 300mA/Cm²
RuO₂, IrO₂, PbO₂, MnO₂, Co₃O₄ ...
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 adapted to perchlorates but degrades faster below 50g/L of chlorate in brine. It is therefore imperative to stop the electrolysis at this time (to prevent fast degradation of Pt Anode).

The cathode (-) :

It is the one who releases hydrogen. This part must simply resist corrosion. Generally cathode is made of titanium (the « Grade 1 », is really better than others), or stainless steel type 304, 316 or 347. Pure platinum also works very well ...

Titanium : for some grades of titanium, (the presence of aluminum in the alloy?) Tends to bend them on the opposite side to the hydrogen bubbles (creation of cavities in the alloy?). Do not use thickness <1mm unless they are held at the edges.

4 - Cell :

A cell is a device that has two electrodes : the Anode (+) and the Cathode (-) immersed in an aqueous brine in a container (total sealing is practically impossible because of the very corrosive chlorine gases).



For chlorate / perchlorate application:

- The container is usually made of glass or pyrex (PE and PP plastics have a lifespan of only a few months. Polymers are not recommended except PTFE)
- There is no need for a separation membrane between the electrodes (used sometimes in the presence of anode graphite, which degrades quickly and contaminates the solution), perhaps with the exception of the PbO₂ coating which gradually disintegrates..
- It is usually necessary to provide a degassing tube for hydrogen gas (+Cl₂).

- The electrodes must be sealed in glue/resin/seal/plastic to prevent the solution from rising by capillarity and quickly attack the connections (in a few days).
- 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 silicones). The author's advice is not to waste time trying.
- The plastic/seals must withstand the temperature of the solution AND Cl₂ gas.
- An electrolysis cell represents a real explosion risk in a closed environment, so use an extraction pipe, fume hood, or outdoor location in a secure area.

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 intruding by capillarity.

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

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 frame makes it possible to resist 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.

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 ?	Test	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	?	No	Probably works for a while

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	

6 - Brine :

Theory :

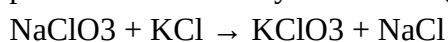
In theory, any chloride can be transformed into chlorate and perchlorate.

In practice difficulties are encountered for certain kind of chlorates/perchlorates : solubility, instability, adhesion on the cathode, rapid decomposition ...

In practice :

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.

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:



The weakly soluble KClO₃ (see table part 2) precipitates and the NaCl remains dissolved.

It becomes possible to filter the KClO₃ 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.

There are a number of types:

→ chromates: sodium/potassium dichromate, ...

→ fluorides: NaF, ...

→ persulfates: sodium, potassium and ammonium.

It is strongly recommended to use a persulfate 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.

Be careful, some types of anodes such as those containing oxides (PbO₂ / RuO₂ / IrO₂ ...) 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.

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.

For that, you need to know the amount of current flowing through the cell per unit of time.

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 adjustable current stabilizer will keep you on a steady current and will adjust the voltage itself to achieve this task.

You just need to set the maximum allowable voltage to output.

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. To adapt according to your knowledge, electrode technology and your specifications or priorities.

A good electrolysis of chlorate with an MMO anode current density 200mA/Cm² is between 3.1 and 3.5V 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 be accelerated.

Equipment :

In 2019 (to be updated), for small inexpensive applications, the author advises you 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 .

For a little more advanced use, 20A modules are strongly recommended, including TO220 mosfets mounted on aluminum radiators.

For those who have a little more money, (or who do not particularly want to hack), use a laboratory power supply : voltage and current regulated, with display, all in one, convenient to use and who have become very affordable, even for 10A max. (about 50 to 70€ including shipping)

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. Does not heat at room temperature, and pauses if the housing rises to 45/60 ° C, as in full sun.

ALL current regulators, in principle, can be paralleled. This makes it possible to infinitely increase the current on a cell, even with small modules.

No destruction of material has ever occurred in this manipulation with many devices.

On the other hand, the inversions of polarity and fusion of the poor connections has burned many of them !

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 0,3/0,5mm² 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.

Clamps :

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 bolt two copper plates, or zinc (or tin), on the electrodes.

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 12 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: $3\text{NaClO} \rightarrow \text{NaClO}_3 + 2\text{NaCl}$.

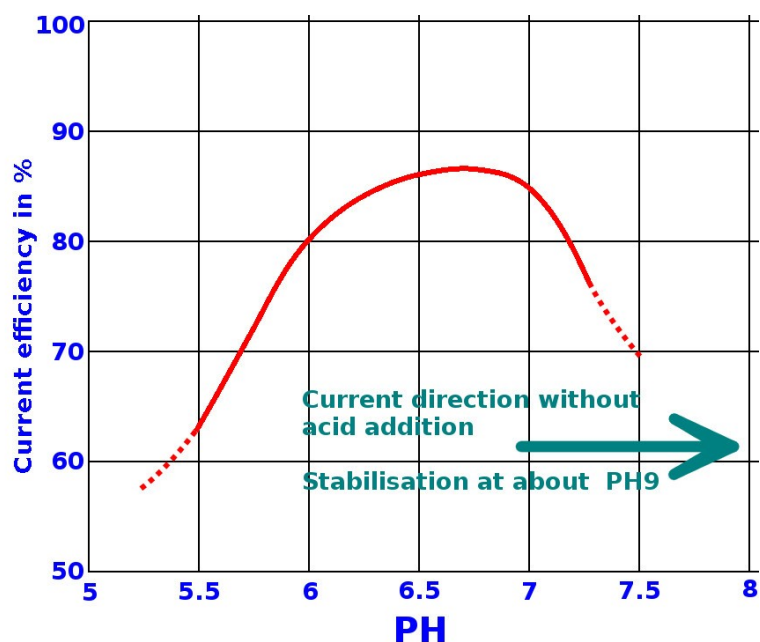
Acidity affects the yield.

Without going into the chemical details, the chlorine that forms and releases itself from the cell produces as much sodium hydroxide (NaOH, KOH, etc.) in the brine that will raise the pH and reduce the yield.

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.

Here is a table:



Conditions : 60°C, magnetite Anode, density :
 30mA/Cm², NaCl : 230g/L, 2g/L Sodium Dichromate.
 From Journal of Electrochemical Technology 6 (1968) 402

9 - Getting started :

Brine preparation :

In reality, it is almost impossible to reach saturation max at the indicated theoretical temperature.

These empirical values can be used in mass by volume of brine:

→ NaCl: 270g / L, about 270g + 860mL of water

→ KCl: 350g / L, about 350g + 830mL of water

- Boil water in a container, then pour in the salt and stir.
- Once the salt is dissolved, (don't care about a small residue) add persulfate (Na, K or NH₄) at a rate of 2 g / L of brine. (2 to 4g according to the sources).
- When the brine is still warm, around 50/60 ° C, pour it into the container and place the lid. (Warning to the thermal shock for the glass)
- Place the lid. It is preferable that a gasket be installed, but it is especially important that the hydrogen gas is released through a suitable orifice, away from any source of flame/spark (risk of explosion).
- Check that the max voltage of the power supply is at 6V max; or according to your experience for your cell apparatus.

Before commissioning, it is better to set the current value to 0. This value can only be read when current flows through the cell. Do not worry, the 6V (or less) initial setting will protect you from excessive current anyway.

f) Put the clamps on the electrodes or connections, (or if possible, bolt the wires to copper connectors).

→ Anode (+): red wire of the power supply on the electrode covered with a dark/black and rough substrate for an MMO anode, or Platinum for the lucky ones.

→ Cathode (-): black wire of the power supply on the titanium or stainless steel electrode.

g) It is important to start the electrolysis at a temperature $>40^{\circ}\text{C}$ to prevent sodium hypochlorite (or other), to form and to release chlorine. The difference is radical, the start almost no longer feels like chlorine, compared to a cold start.

h) Once started, check and adjust the current flowing through the cell.

It is normal, for a good start from 3.4V +/- 0.2V then the voltage increases (your regulator adapts) during the first minutes to 4 to 4.5V.

i) If the assembly is well done, putting your nose on the hydrogen outlet you will feel almost no smell of chlorine. Otherwise, you have room for improvement.

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 $\text{PH}>9-10$ and the voltage may rise to more than 5.5V between electrodes for MMOs. It is better then to cut it, because you would quickly destroy the anode, and start it again by adjusting the PH with HCl.

j) In the following days, check the voltage, (the current will be constant, fixed by the module) the level of the brine that evaporates, the temperature, the connection of the clamps (heating?) and the possible degradation of the Anode.

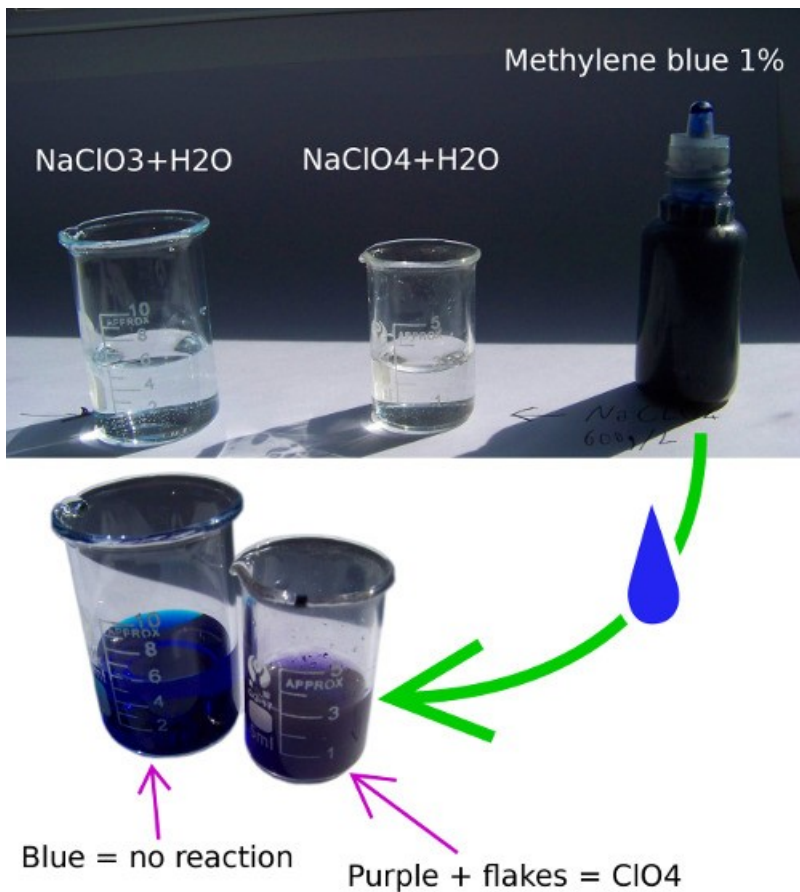
k) Add water as the liquid evaporates. Evaporation is a normal phenomenon.

l) 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 ...)

m) Once the theoretical time has elapsed to reach the end of the chlorate (see part 10 below), it must be tested to see if there is presence of perchlorate. Drop a drop of 1% methylene blue (for example) 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 :

Electrolysis of chlorate:

$$6 \text{ coulombs/mol (2 coulombs/mol oxygen)} = 96\,485 \cdot 6 \text{ mol} / 3600 \text{ Sec} = 160.8 \text{ A/H/mol}$$

$$\text{NaCl} \rightarrow \text{NaClO}_3 = 2.752 \text{ A/H/g NaCl in brine} = 1.511 \text{ A/H/g final gram of chlorate}$$

$$\text{KCl} \rightarrow \text{KClO}_3 = 2.157 \text{ A/H/g of KCl in brine} = 1.312 \text{ A/H/g final gram of chlorate}$$

In other words : if the NaCl brine is traversed by 2.75 amperes for 1 hour, 1 g of NaCl will disappear and will be changed to 1.821 g of sodium chlorate in the molar ratio between NaCl and NaClO₃.

Perchlorate electrolysis: (in one step) :

$$8 \text{ coulombs/mol (2 coulombs/mol oxygen)} = 96\,485 \cdot 8 \text{ mol} / 3600 \text{ Sec} = 214.4 \text{ A/H/mol}$$

$$\text{NaCl} \rightarrow \text{NaClO}_4 = 3.669 \text{ A/H/g of NaCl in brine} = 1.751 \text{ A/H/g final gram of perchlorate}$$

$$\text{KCl} \rightarrow \text{KClO}_4 = 2.876 \text{ A/H/g KCl in brine} = 1.548 \text{ A/H/g final gram of perchlorate}$$

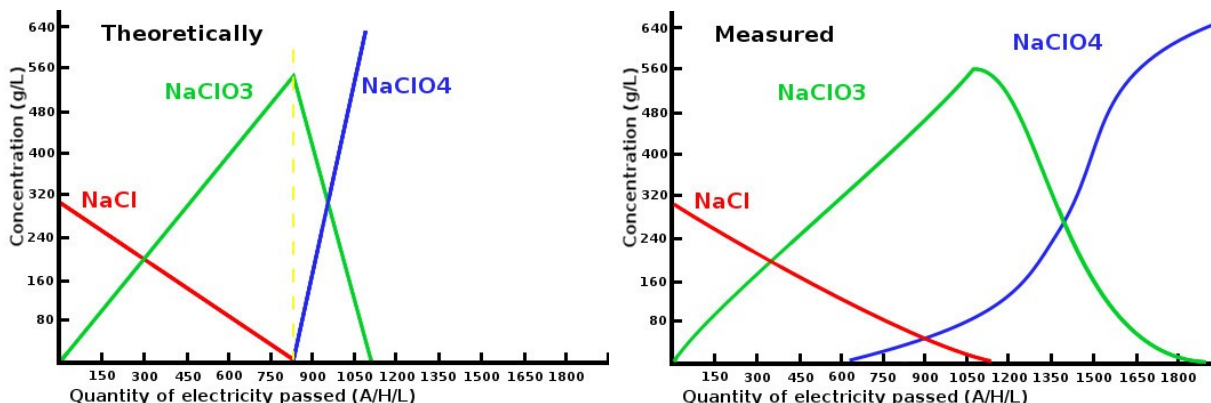
(Perchlorate need higher current density. It is more difficult to obtain than chlorate for different technical reasons.)

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 40-50%.

A good amateur cell goes up to 80%.

Two theoretical and practical comparative tables :



We can see that the formation of perchlorate is not simultaneous with the disappearance of NaCl.

An empirical solution to obtain chlorate is to continue the electrolysis of two-thirds of the time already elapsed to the apparition of violet under the drop of methylene blue.

The slight rise of the voltage can be an indicator of perchlorate formation.

But this indicator can be unfortunately also due to other factors : oxidation of the cathode, changing PH, temperature, oxidized connections ...

NaCl example :

Per hour				
Current	Yield 50 %		Yield 80 %	
	NaCl consumption	NaClO3 produce	NaCl consumption	NaClO3 produce
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 NaCl remains in the end, if you stop at chlorate. It is close to 2% of the initial chloride in 50% yield but much more in 80% yield.

It is therefore necessary to continue the electrolysis beyond this time if you want to reach a final low rate of 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".

The operation consists of starting from a soluble salt such as NaCl and adding, once the chlorate or perchlorate obtained, 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 : $\text{NaClO}_3 + \text{KCl} \rightarrow \text{KClO}_3 + \text{NaCl}$

Several reasons justify this operation in favor of NaCl salt :

- The solubility of NaCl, and even more of its chlorate and perchlorate
- The possibility of filtering the brine when it is soiled by deposits of the anode (graphite PbO_2 , see MMO) and obtain pure crystals after metathesis.
- The health aspect and non-danger of NaCl, compared to other salts (NH_4Cl ...)
- The technical control of this type of electrolysis easier than other salts (BaCl ...)
- The low cost of NaCl
- The infinite recycling facility of the initial brine
- Mandatory for certain insoluble perchlorate (KClO_4), therefore impossible to obtain directly

For this, 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 the solution as low as possible to 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.

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

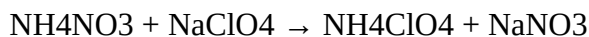
- 1 - Prepare 127.6g of KCl in powder.
- 2 - Add this mass of KCl in the electrolyzed brine still hot (heat is important for solubility).
- 3 - Stir until a very fine homogeneous powder is obtained in the container.
- 4 - Put in a very cold place (fridge, freezer ...)

5 - Filter the white crystals in suitable filter: cloth, coffee filter, laboratory filter ...

Ammonium Perchlorate NH₄ClO₄ :

(One of the possible and effective methods)

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



For 1mol (example):

→ 1 mol of NaClO₄ = 122,44g

→ 1 mol of NH₄NO₃ = 80,04g

→ 167mL of water

Dissolve the two anhydrous powders in water (distilled), and stir. A white powder rushes.

Cool to 0°C to optimize the precipitation yield.

Filter it. Result : 83.6% of NH₄ClO₄ crystals are obtained by this way at 0°C (from 77 to 84% depending on the temperature of 5 to 0°C).

At 0°C only 0.164mol/167mL of NH₄ClO₄ can dissolved against 1.43mol/167mL for NaNO₃ at 0°C. It is therefore possible to lower the volume of water a little more.

12 - Chemical properties :

Properties of chlorates :

Chemical formula : NaClO₃/KClO₃

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 : NaClO₄ and KClO₄

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 NaClO₄) 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.