

Chemicals from Salt: Teacher Notes

Brine

Aqueous solutions of sodium chloride and potassium chloride are both referred to as brine in the industry.

Diaphragm cells

Diaphragm cells, as well as membrane cells and flowing mercury cathode cells, are used for the electrolysis of brine (comparison of cell types shown in the table below). The essential design feature of all three types of cell is that the chlorine produced at the anode must be separated from the sodium (or potassium) hydroxide produced in the electrolyte or the two will react together to form sodium (or potassium) chlorate(I) (sodium (or potassium) hypochlorite):



The basic principle of the diaphragm cell is similar to that of membrane cells but an asbestos diaphragm is used to separate the anode and the cathode compartments. Brine actually flows through this membrane so that the sodium (or potassium) hydroxide produced contains significant amounts of chloride. This diaphragm has to be changed every 100 days or so, compared with the life of up to three years for the membrane of a membrane cell.

For these reasons new diaphragm cells are unlikely to be constructed, but existing ones will continue in production to the end of their useful lives after which they will probably be replaced by membrane cells. The same is true of flowing mercury cathode cells.

Membrane cells are very flexible in use. Cells can be connected together to give whatever capacity is required. Small users of chlorine, such as paper mills (where chlorine is used as a bleach), can have one or two cells working on site.

Table: A comparison of membrane cells, diaphragm cells and flowing mercury cells (taken from the teacher's notes which accompany the *Discoveries in Science* poster series produced by ICI).

Cell type	Construction	Operation of cell	Quality of NaOH produced
Diaphragm cell	Relatively simple and inexpensive.	Frequent replacement of diaphragm. Constant current load needed. Operates at 3.8 V.	Must be evaporated to concentrate to 50% and to crystallise out salt.
Mercury cell	Expensive to construct and charge with mercury. Needs a large floor area.	Mercury is potentially hazardous and must be reclaimed from any effluent. Can operate over a wide current load. Operates at 4.5 V.	High purity. Produced at 50% concentration.
Membrane cell	Cheap to construct and install.	Requires high purity brine (low Ca, Mg). Can operate at varying current loads. Operates at 3.3 V. Membrane change every 2-3 years.	High purity. Must be evaporated to 50% concentration.

Solution mining

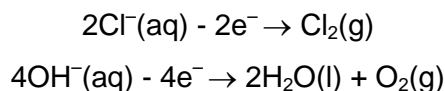
Solution salt mining takes place in the Cheshire salt field near Northwich, about 12 miles south east of Runcorn.

Brine wells must be constructed sufficiently far apart to avoid the possibility of collapse.

Some old solution mining cavities are used to store natural gas.

Anode reactions

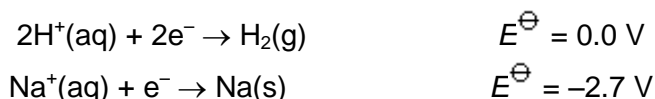
There are two possible reactions at the anode:



Hydrochloric acid is added to the brine to reduce $[\text{OH}^-]$ and suppress the second reaction which is not required.

Cathode reactions

The two possible cathode reactions are:



Under standard conditions (*ie* with a platinum electrode for hydrogen), the former occurs in preference to the latter due to the more positive discharge potential. This is what occurs in the membrane and diaphragm cells. However, with a mercury cathode there is a high overvoltage which prevents the discharge of hydrogen. Overvoltage is a kinetic phenomenon which slows down the transfer of electrons to hydrogen ions. Thus sodium is discharged rather than hydrogen. The discharged sodium forms a solution in the mercury (an amalgam) with a concentration of up to 0.5%.

The sodium in the amalgam does not react with the water in the brine because there is no graphite catalyst present. Graphite is used to speed up the reaction in the denuder.

Removal of calcium and magnesium ions from brine

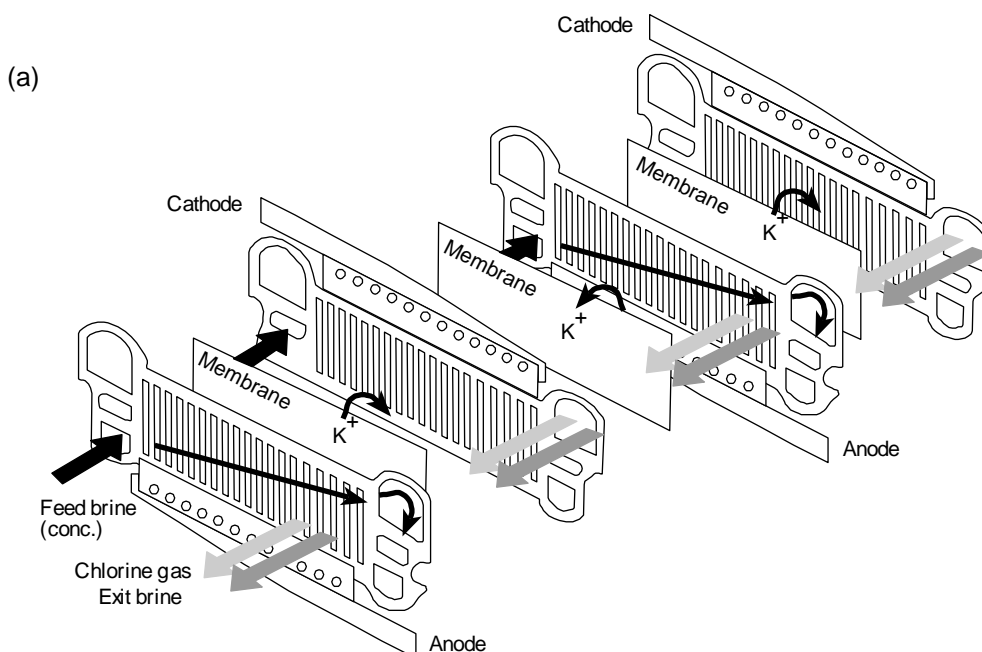
These ions are removed by precipitation. Sodium carbonate and sodium hydroxide solutions are added to precipitate out calcium ions as insoluble calcium carbonate, and magnesium ions as insoluble magnesium hydroxide. The precipitates are then removed by settling and filtration.

Membrane cell construction and operation

This is quite complex (see figure). Brine (potassium chloride solution in the cells in the video clip, but other cells electrolyse sodium chloride solution) is fed into the cell and flows along the anodes where some chloride ions are discharged as chlorine. At the same time, potassium ions pass through the membrane into the cathode compartment. The combined effect is to make the brine more dilute. Chlorine gas is swept out of the cell by the dilute brine solution and separates out in a simple T-junction (figure 1(a)).

Dilute potassium hydroxide solution is fed into the cell and flows along the cathodes where water is decomposed into hydrogen gas and hydroxide ions. The hydroxide ions, together with the potassium ions which pass through the membrane, form a more-concentrated solution of potassium hydroxide. This sweeps hydrogen from the cell which separates from the potassium hydroxide solution at a T-junction (figure 1(b)).

The membrane is permeable to cations but not anions. It is based on poly(tetrafluoroethene) (PTFE) with anionic side chains ($-\text{SO}_3^-$ and $-\text{COO}^-$) which repel anions. The hydrated cations carry some water through the membrane.



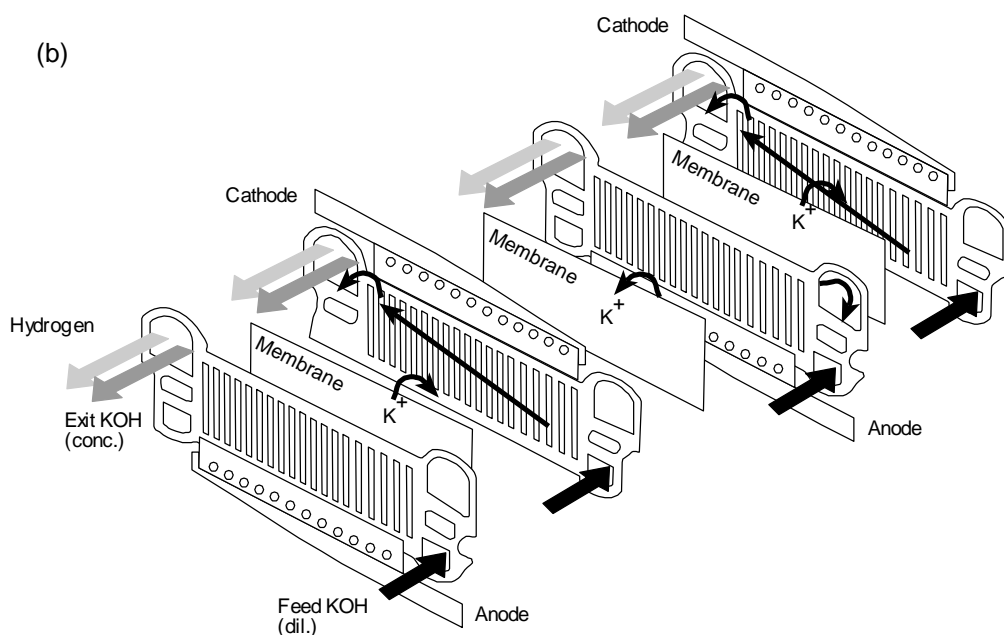


Figure 1: Membrane cell construction and operation as described above.

The important teaching point is that in the anode compartments the brine becomes less concentrated due to discharge of Cl^- ions and loss of K^+ ions through the membrane. In the cathode compartments, dilute potassium hydroxide solution is fed in and becomes more concentrated as OH^- ions are produced and K^+ ions arrive through the membrane.

Membrane cells can electrolyse sodium chloride or potassium chloride solutions. For sodium chloride, the dilute brine is discharged into the river estuary – it is much less polluted than the water already there! Potassium chloride is more expensive, and the dilute solution is re-saturated by adding more of the solid salt. The hydroxide solutions, called ‘caustic’, are diluted or evaporated as required by the customer.

Sodium chloride comes on site as an aqueous solution transported by pipeline from the Cheshire salt fields. Potassium chloride is brought from the north east as a solid and dissolved in water on site. It would be inefficient to transport a solution of potassium chloride, which is mostly water, by tanker and a pipeline would be too long.

Testing the chlorine

The sampled chlorine is tested by gas chromatography to check for contamination by hydrogen, oxygen and carbon dioxide. The presence of any of these indicates problems with the cell:

- hydrogen suggests that the membrane needs replacing;
- oxygen that there is a problem with the anode; and
- carbon dioxide suggests that there is an air leak.